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Analysis System for Total Sulfuric Acid in Ambient Air. Development and Preliminary Evaluation

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Springfield, VA

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ANALYSIS SYSTEM FOR TOTAL SULFURIC ACID IN AMBIENT AIR

Development and Preliminary Evaluation

by

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ABSTRACT

A total sulfuric acid analysis (TSAA) system was developed and shown to provide quantitative determinations of sulfuric acid in air at concentrations as low as 0.26 $\mu g/m^3$. Quantitation at lower concentrations appears to be possible. The general approach in the design and development effort emphasized sample conditioning, rather than detector selectivity, to provide unambiguous detection. Separation of the acid from other sample components was accomplished by stagewise condensation and revaporization; therefore particulate filters were not required. The efficiency of this approach was compared to a manual approach which involved sampling sulfuric acid mist in air by means of glass fiber filtration, and analysing for sulfuric acid by pH determination. The results of the comparative study indicated that the TSAA system was as efficient in its determination of sulfuric acid mist in air as the manual approach. Effects of major potential interferences (SO_2, NH_3, and ammonium sulfates) apparently were eliminated by the addition of a small amount of hydrogen chloride to the sample.

This report was submitted in fulfillment of Contract No. 68-02-2465 by Versar Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 30, 1976 to April 17, 1980, and work was completed as of April 17, 1980.

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1.0 INTRODUCTION

1.1 Statement of Program Purpose

To date there appears to be only one acceptable way of determining sulfuric acid (H_2SO_4) in ambient air. The method (or methods) consists of exposing a filter matrix to large quantities of air and determining from this filter matrix the total quantity of collected sulfate ions (by x-ray diffraction) and hydrogen ions (by pH). Although the method appears to be the most valid technique available, it does suffer from serious drawbacks; it requires lengthy procedures and the support of a well-equipped laboratory. For these and other reasons, EPA has been in search of instrumental techniques which display the following characteristics:

1. Extreme sensitivity to low level H_2SO_4 as it exists in ambient air (less than 1.0 $\mu g/m^3$).
2. Specificity for the H_2SO_4 molecule as opposed to its separate ions.
3. Freedom from ambient (and analytical) interferences.
4. Ability to be easily incorporated into a hardware system.

In addition, any instrumental technique manifesting the above characteristics in the analysis of H_2SO_4 should possess its own calibration subsystem.

From the outset of this program with EPA under Contract No. 68-02-2465, our primary purpose has been to develop a total sulfuric acid analysis system which would exhibit all the above characteristics.

1.2 Comments on Versar's Approach

There are several approaches that have been taken in the pursuit of an instrumental method for the valid measurement of H_2SO_4 in environmental air samples. In general, however, the many approaches pursued can be reduced to <u>two</u> basic approaches which are related to the question, "What portion of the analyzer system should receive the majority of development?" One basic

approach would be to emphasize development of a detector subsystem which would be both sensitive and selective for molecular H_2SO_4. Indeed, if such a detector were developed, then it would follow that the sample handling subsystem (area between source and detector) would require less developmental effort. The other approach is to place more emphasis on developing sample handling subsystems and less on the detector. This approach would allow the use of conventional detectors downstream of the sampling handling subsystem.

Obviously, there are many problems that have to be overcome with either approach. The former, the detector development approach, would be the ideal approach. Such an approach may result in a system which could cause minimal changes to ambient H_2SO_4 in addition to better approximation of the atmospheric "real time" changes in the concentration of H_2SO_4. However, there appear to be formidable problems to be overcome in this basic approach, the most serious of which is related to a lack of knowledge concerning the exact form in which H_2SO_4 exists in the ambient. If H_2SO_4 existed in a purified liquid droplet form (such as is generated by an atomizer acting on a solution of H_2O and H_2SO_4), then the development of such a detector might be feasible. But ambient H_2SO_4 does not appear to exist in a purified form of droplets containing only H_2SO_4; rather, it probably exists as a heterogenously mixed particle which may contain other sulfate forms such as ammonium acid sulfate (NH_4HSO_4), ammonium sulfate ($(NH_4)_2SO_4$) and metals in addition to H_2O and unreacted H_2SO_4. A detector with specificity to molecular H_2SO_4 would be required to sort out unreacted H_2SO_4 from a heterogenously mixed particle contained in a fast moving air stream. To further complicate matters, the detector would be required to quantitate H_2SO_4 to an extremely low level, on the order of 2.5×10^{-5} ppm or 0.1 $\mu g/m^3$.

The latter approach, with emphasis on sample handling, seemed to Versar to be the more reasonable approach with a much higher expectation of success. It was our belief that the level of developmental effort should be rightfully placed on the sample handling subsystem (upstream from the detector). It is in this area of the analysis system that (1) the system would be rendered specific for molecular H_2SO_4 using, for example, a conventional FPD

for the total sulfur detection and (2) H_2SO_4 may be concentrated to satisfy the quantitative requirement of the system without concentrating other interfering species.

Versar has had significant success in developing a sulfuric acid analysis system using this approach, as evidenced by the results and data presented in this report.

1.3 History of the Program

On September 30, 1976, Versar was awarded an EPA contract (68-02-2465) with an overall objective of designing and fabricating a sampler with a capacity of removing H_2SO_4 from a sample stream without the occurrence of sample degradation caused by interaction of the H_2SO_4 with other ambient particulate and/or gaseous species. Furthermore, the sampler should be capable of being integrated with a flame photometric detector (FPD) for analysis of the H_2SO_4. In addition, upon completion of fabrication, the sampler was to be preliminarily evaluated to determine sampling efficiency and to demonstrate that the sampler does not suffer from interferences due to species such as sulfur dioxide (SO_2), ammonia (NH_3), and ammonium sulfates.

The sampling concept, designed to eliminate the interferences suffered by conventional sampling system, involved a process of collecting H_2SO_4 in the absence of particulate and gaseous interferences. The sampler was to perform collection, transport, and sample conditioning processes and was to be developed for use with the FPD. The approach involved heating the sample air, immediately upon its entering the sample duct, to a temperature above the dewpoint of H_2SO_4 mist and filtering the heated sample air for the removal of solid particulates within the same physical duct. The vaporized H_2SO_4 acid mist was then to pass through the same filter unaffected and to be swept into a cooled compartment where the temperature would be rapidly reduced to the ambient level. At this temperature, the H_2SO_4 should condense to reform the mist for subsequent removal from the air stream by a second filter. During the next phase of operation, the sample compartment of the sampler was to be flushed with clean air for the subsequent removal of NH_3 and sulfur bearing gaseous species. The final step of operation involved the vaporization of the

collected sulfuric acid and transport of the H_2SO_4 vapor to the FPD for sulfur measurement. Presumably, at this point in the processing, all the airborne sulfur reaching the FPD should represent the H_2SO_4 originally collected during the sampling phase.

An instrument was built incorporating all these design features and was preliminarily evaluated for the quantification of H_2SO_4. The results of the preliminary evaluation indicated that the H_2SO_4 was not being transported quantitatively throughout the sampler; it appeared that the wall materials of the sampler were interacting with the H_2SO_4. The instrument, which consisted of the sampler and FPD, were transported to the facilities of the USEPA, Research Triangle Park, North Carolina, where it was demonstrated on a low level source of H_2SO_4 mist. The results of the demonstration indicated the need for more design effort on the sampler system, especially in the area of material selection. This additional effort was initiated in 1977.

One of the first efforts on the modified program was to evaluate several materials with respect to transport properties of H_2SO_4. The list of materials examined included PTFE Teflon, FEP Teflon, gold plated copper, stainless steel, untreated and silanized pyrex glass, untreated and silanized quartz glass, FEP Teflon-coated stainless steel, and silicone. Of these materials, PTFE Teflon and silanized glass appeared to have the least wetting and wall retention problems associated with transporting H_2SO_4.

It was at this juncture of the program that several changes were made in the original design of the sampler. These changes are summarized below:

1. It was necessary to design in terms of a total H_2SO_4 analysis (TSAA) system as opposed to narrowing our scope of development to just the sampler. Because of the seriousness of the problems associated with transport of H_2SO_4, the overall design of a complete TSAA system was considered from the start in order to avoid any future problems associated with integration of the subsystems.

2. The internal walls of the sampler and FPD pneumatic lines were constructed of PTFE Teflon or silanized glass.

3. The first and second filter in the sampler subsystem were not included in the next fabricated instrument so as not to complicate system operation. This also served to produce a baseline for evaluation of the effectiveness of these filters.

4. The control box was rendered more flexible in design so as to allow for variability of penumatic function in the overall operation of the system. This simplified the evaluation of the TSAA system.

5. A calibration subsystem (including a commercially available atomizer) was designed into the TSAA system to provide means for challenging the system against low levels of H_2SO_4 mist.

6. High velocity sampling was designed into the total analysis system to: (1) increase the sensitivity of the system to ambient H_2SO_4 and (2) minimize wall deposition of H_2SO_4 and other particulates on the internal walls of the TSAA system.

7. Electrically operated solenoid valves were eliminated from the high temperature oven (containing the sample transport duct, collection chamber, and FPD). During the course of evaluating the first instrument, the high temperature solenoid valves exhibited excessive failure rates which led to severe maintenance problems in the sampler.

The TSAA system incorporating the above design features was designed, fabricated, and evaluated. The results of this preliminary evaluation indicated successful quantitative measurement of sulfuric acid, but the TSAA system

did exhibit some problems. The H_2SO_4 peaks were not symmetrical, and the peaks demonstrated memory effects. In addition, preliminary evaluation of NH_3 and SO_2 interference effects indicated that these effects were significant.

The instrument and associated hardware were set up and demonstrated at the EPA facility in Research Triangle Park in September, 1979. The results were encouraging only insofar that successful quantitation of H_2SO_4 entering the system appeared to have been realized. Since that time, work has continued on the system under in-house sponsorship by Versar.

Results obtained in late 1979 and early 1980 have shown that:

1. The incorporation of a humidifier into the system, which served to bring the water content of the carrier gas to near saturation, results in reproducibly quantitative removal of the acid from the chamber walls, elimination of the memory effects, and reduction of acid elution times to 3-6 minutes from the 15-20 minutes observed with dry air;

2. Quantification of acid has been demonstrated at sample concentrations (H_2SO_4 in air) as low as 0.26 $\mu g/m^3$, and quantification appears to be available at acid levels as low as 0.06 $\mu g/m^3$;

3. Interference from NH_3, SO_2, NH_4SO_4, and $(NH_4)_2SO_4$ can be eliminated through addition of a relatively low concentration (on the order of 100 ppm) of hydrogen chloride (HCl) into the sample; and

4. Particulate filters are not required in the system. In addition to eliminating the potential for plugging and acid reaction with trapped particulates, the absence of filters in the sampling line also facilitates maintenance of a constant system flow impedance.

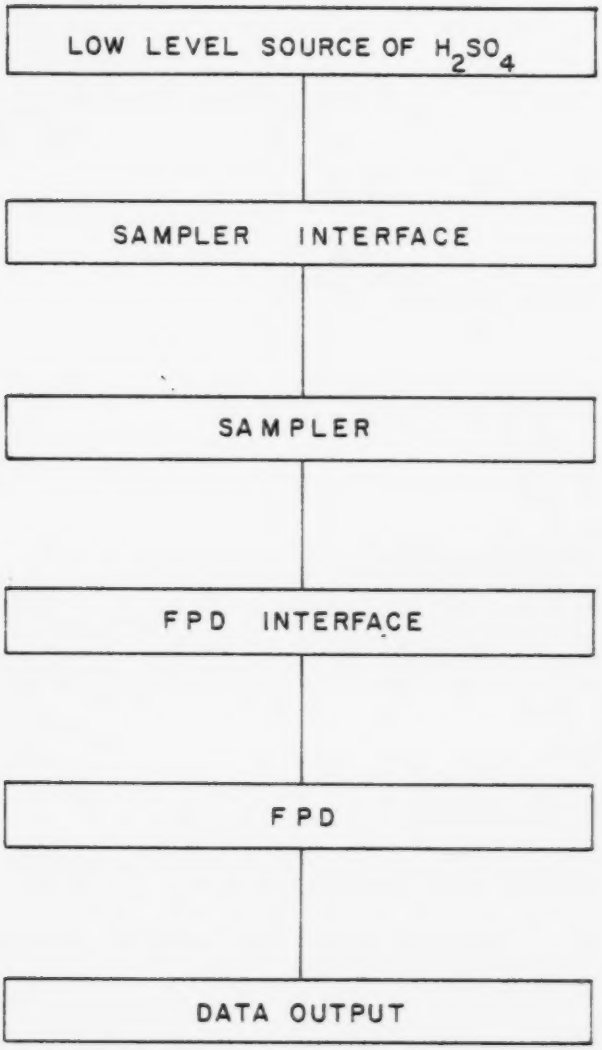

FIGURE 1

BLOCK DIAGRAM OF TSAA SYSTEM

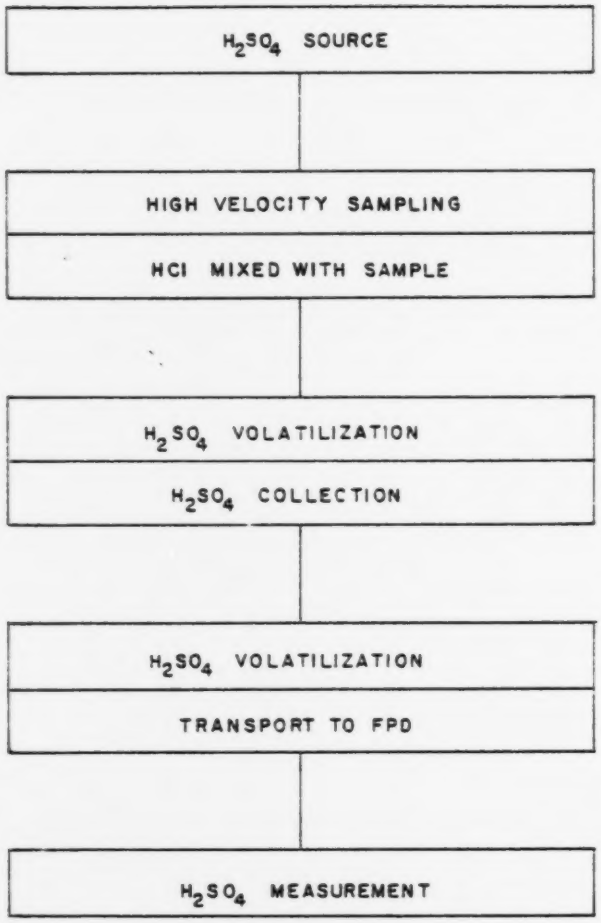

FIGURE 2

BLOCK DIAGRAM OF METHODOLOGY OF TSAA SYSTEM

2.0 TECHNICAL DISCUSSION

The technical aspects of system methodology, system description, evaluation methods, and results of the evaluation are discussed in detail in this section of the report.

2.1 Brief Description of the TSAA System and H_2SO_4 Measurement Methodology

Block diagrams of the TSAA system and measurement methodology are presented in Figures 1 and 2, respectively. In general, there are two operation modes per analysis cycle when measuring H_2SO_4 with the TSAA system. The operation modes are sampling and analysis, which are briefly discussed below. The source of the sample gas can be low level H_2SO_4 emanating from an atomizer (such as the Baird-Atomic used in this program for evaluation) or it can be ambient air. In the discussion below it is assumed that the source stream is ambient air.

2.1.1 Sampling

Starting with the ambient air source of H_2SO_4, sample air is pulled into the hot transport duct of the TSAA system where it is mixed with a low level of hydrogen chloride (HCl) gas. *The importance of the HCl gas is that it prevents sulfur dioxide (SO_2) and ammonia (NH_3) from interfering with the (later) measurement of H_2SO_4.* The sample stream containing the HCl gas travels down the bore of the hot transport duct and is heated rapidly to a temperature approaching 400 F during which the H_2SO_4 is volatilized. The sample stream containing H_2SO_4 in the vapor state enters the collection chamber where it is quickly cooled down to 55°F. At this point in the TSAA system, the H_2SO_4 is condensed and collected on the cool walls of the collection chamber. The sample stream less the H_2SO_4 is then swept from the collection chamber, forced through a charcoal bed where the HCl gas is removed from the sample stream, and exhausted.

It is important to note that the sample stream is forced to flow at a velocity of the order of 30 ft/sec, in order to minimize the deposition of particulates common to the sample stream. In addition, the wall passages of the TSAA system are smooth and without bends to further expedite the passage of unwanted particulates.

2.1.2 Analysis

At the start of the analysis mode of operation, air saturated with water vapor is forced to pass through the hot transport duct and into the collection chamber, which is now heated to a temperature approximating 400°F. In this temperature regime, H_2SO_4 is volatilized off the walls of the chamber and is passed to the FPD for the measurement of H_2SO_4.

Air saturated with water vapor is necessary for the quantitative removal of H_2SO_4 off the hot walls of the collection chamber. Dry air will not allow the quantitative removal of H_2SO_4.

The time required to perform both sampling and analysis functions depends on the level of H_2SO_4 in the ambient air. For levels of the order 10 $\mu g/m^3$, approximately six minutes are required to complete the entire cycle, 3 minutes for sampling and 3 minutes for analysis.

2.2 Detailed Description of the TSAA System

The TSAA system can be functionally described in terms of its six major subsystems, which include the low level H_2SO_4 generator, the sampler interface, the sampler, the FPD interface, and the FPD. These subsystems are described pneumatically in Figure 3. Each of the subsystems performs specific tasks which are important to the overall success of the analyzer system. Table 1 presents the parts list for the TSAA system, keyed to the numbered components on Figure 3.

2.2.1 Artificially Produced Low Level H_2SO_4

A constant low level source of H_2SO_4 is required for check-out of the TSAA system. Levels ranging from 0.25 to 10 $\mu g/m^3$ in air have been artificially produced for this purpose. The major components of this subsystem (as constructed by Versar) are the air filtration assembly, Baird-Atomic atomizer, and the pressure and flow control pneumatics. The purpose of the air filtration assembly is to supply chemically clean makeup air to the Baird-Atomic atomizer for its atomization of dilute H_2SO_4 in H_2O. In addition to being chemically clean, the air must also be extremely dry in order to prevent

TABLE 1. PARTS DESCRIPTION - TSAA SYSTEM

1. Cross Connector
2. Two-way electrically operated n.c. solenoid valve
3. Pressure regulator
4. Pressure gauge
5. Dilute H_2SO_4 solution
6. Baird-Atomic atomizer
7. Manometer
8. Cross connector
9. Tee connector
10. Cross connector
11. Activated charcoal bed
12. Same as (2)
13. Flow regulator
14. Low level source HCl
15. Two-way electrically operated n.c. all Teflon solenoid valve
16. Same as (2)
17. Flow regulator
18. Humidifier
19. Tee connector
20. Same as (15)
21. Hot inlet transport duct
22. Sampler oven
23. H_2SO_4 collection chamber
24. Metal compartment
25. Tee connector
26. Flow meter
27. Flow regulator
28. Same as (2)
29. Pressure surge eliminator
30. FPD burner block
31. Photomultiplier tube
32. Heat exchanger
33. Flow meter

TABLE 1. PARTS DESCRIPTION - TSAA SYSTEM (CONTINUED)

34. Flow regulator
35. Pressure regulator
36. Compressed hydrogen
37. Flow regulator
38. Tee connector
39. FPD flow controller oven
40. Fixed impedance orifice
41. Vacuum regulator
42. Vacuum pump
43. Three-way electrically operated solenoid valve
44. Tee connector
45. Two-way electrically operated n.o. solenoid valve
46. Same as (2)
47. Flow regulator
48. Tee connector
49. Same as (2)
50. Same as (2)
51. Liquid separator
52. Tee connector
53. Vacuum pump
54. Same as (2)

Source: "Handbook of Chemistry and Physics", Physical Constants of Organic Compounds, 47 Edition, Page C158, Compound Number b536 (m-Dichlorobenzene), Chemical Rubber Company.

"Handbook of Chemistry and Physics", Physical Constants of Organic Compounds, 47 Edition, Page C166, Compound Number b787 (Hexachlorobenzene), Chemical Rubber Company.

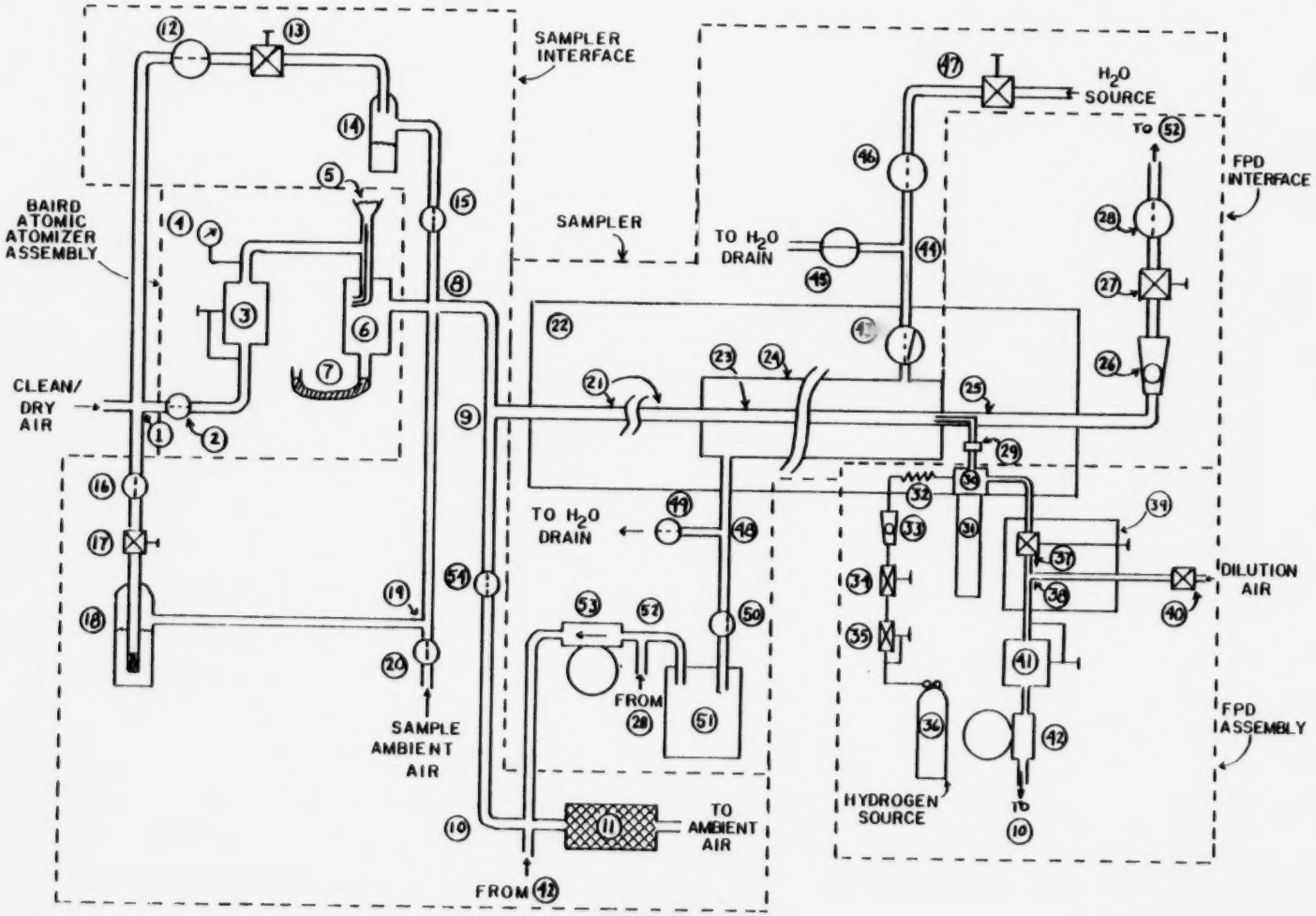

FIGURE 3

PNEUMATIC DIAGRAM OF TSAA SYSTEM

fluctuations in relative humidities which affect H_2SO_4 levels in the aerosol produced by the atomizer. The quantity of clean air required is on the order of 20 l/min (liters per minute). In addition to supplying the atomizer, the air filtration assembly also supplies approximately 0.5 l/min of clean and dry air to the sampler (via the humidifier) during the analysis mode of operation of the TSAA system.

Figure 4 shows the components of the air filtration assembly, which consist of a compressor, heat exchanger, liquid separator, two silica gel beds, an activated charcoal bed, and a particulate filter. Ambient air is drawn into the compressor and is exhausted to a heat exchanger for the cooling of the hot air produced by the mechanical action of the compressor. The pressure on the exhaust side of the compressor is approximately 40 psig. Referring again to Figure 4, the air enters a liquid separator where condensate is removed by impaction from the stream. From the separator, the air stream is passed through a silica gel bed for the removal of sulfur bearing gases and hydrocarbons. Upon leaving the bed of activated charcoal, the air is passed through a second silica gel bed to dry the stream further. The dry air is filtered by passage through a depth filter for its final treatment.

The Baird-Atomic atomizer is manufactured by Baird-Atomic, Inc., located in Cambridge, Massachusetts. The atomizer consists of a spray nozzle, a holder, and a mount. Their part numbers are BA02561, BA02503, and BA02079, respectively. A schematic illustration of the atomizer assembly is displayed in Figure 5.

Referring again to Figure 3, the artificial production of low level H_2SO_4 mist is accomplished by opening solenoid valve (2)* which allows the clean/dry air from the air filtration system to enter a pressure regulator where the air pressure is controlled at a constant pressure of 5 psig. The air is then passed through the spray nozzle section of the atomizer which causes the aspiration and atomization of dilute solution of H_2SO_4 inside the

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*Numbers in parenthesis in this section refer to numbered parts or points in Figure 3.

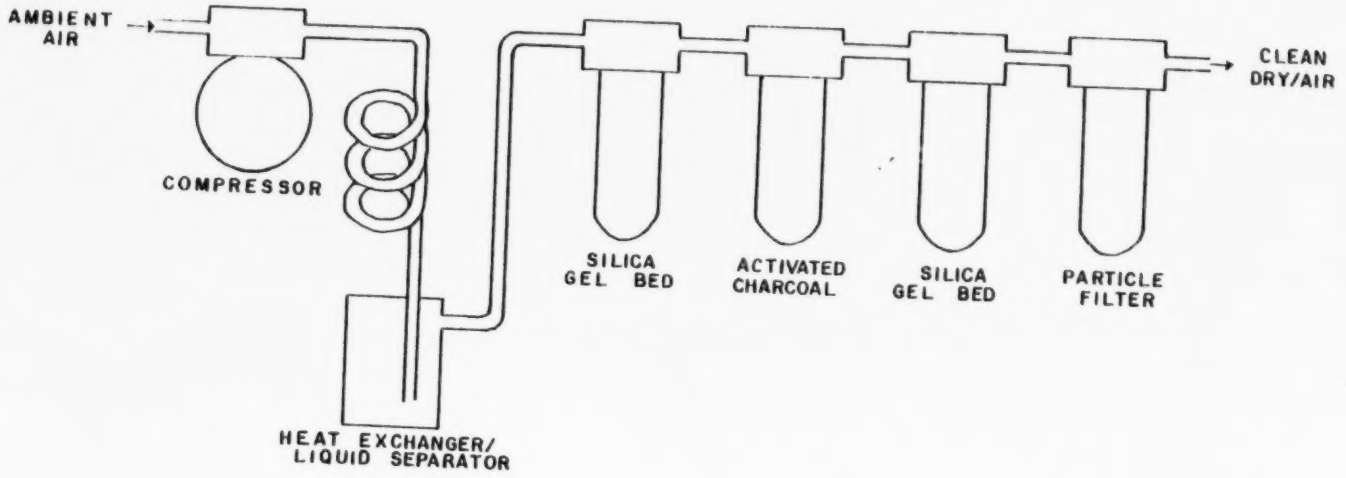

FIGURE 4

CLEAN/DRY AIR ASSEMBLY

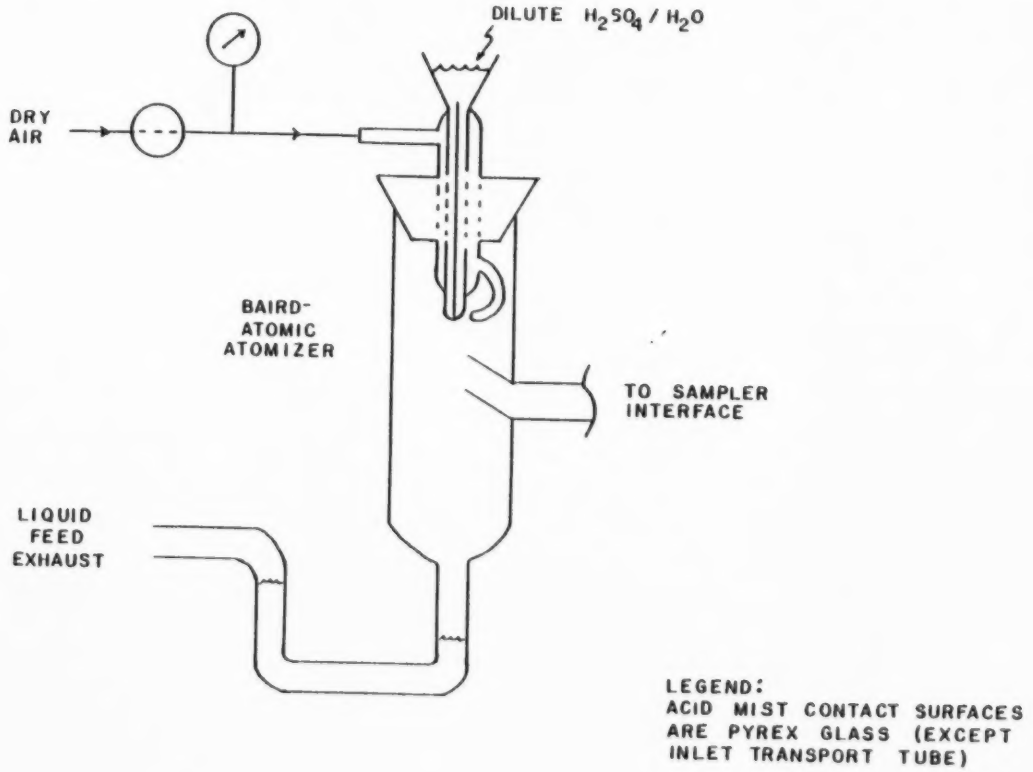

FIGURE 5

DIAGRAM OF B/A H_2SO_4 MIST DELIVERY SYSTEM

cylindrical holder. Most of the aerosol cloud, after production, is impacted onto the internal walls of the holder and is allowed to drain from the holder. A small portion of the aerosol, along with the air stream, is directed out of the holder to the sampler interface.

2.2.2 Sampler Interface

That portion of the TSAA system located upstream from the sampler and downstream from the source of sample air or low level H_2SO_4 is the sampler interface. Its function is to direct the proper streams to the hot transport duct of the sampler during the separate operational modes of the TSAA system.

In the check-out portion of the sampling, the sampler interface directs low level H_2SO_4 and HCl gas in air (from the atomizer) to the hot transport duct, at which point a portion of the stream is drawn into the duct. The excess is evacuated from the sampler interface subsystem via solenoid valve (54) and the activated charcoal bed (11). The HCl gas is mixed with the low level H_2SO_4 stream at point (8) in Figure 3. The delivery of HCl gas is accomplished by the opening of solenoid valves (12) and (15).

During the sampling mode, sample air from an ambient source along with HCl gas is directed to the hot transport duct of the sampler. Unlike the check-out procedure, however, there is no excess sample gas, since all the sample is taken in by the sampler. To accomplish the flow-in of all sample air containing HCl gas to the hot transport duct, solenoid valves (20), (28), (12), and (15) are opened to flow, while solenoid valves (2), (16), (50), and (54) are closed.

In the analysis mode, the sampler interface supplies carrier gas, saturated with moisture, to the hot transport duct where a portion of it is drawn into the sampler. The excess is evacuated from the sampler interface. The flow of carrier gas is accomplished by opening solenoid valves (16) and (54) while closing solenoid valves (2), (12), (15), and (20).

2.2.3 Sampler

The sampler subsystem, shown between the sampler interface and the FPD interface on Figure 3, is responsible for the removal of H_2SO_4 from either

the sample stream or the low level source stream, both emanating from the sampler interface. In addition, it is responsible for the volatilization of H_2SO_4 and for its transport to the FPD interface subsystem. The sampler consists primarily of the hot transport duct (21) and the collection chamber (23) which are both maintained at controlled temperature in an insulated oven (22). The hot transport duct consists of a 2-foot run of ¼-inch O.D. thin-wall PTFE tube. It is in this tube that the H_2SO_4 is volatilized for eventual extraction from the stream by forced condensation in the collection chamber.

The collection chamber consists of a 3-foot run of ¼-inch O.D. thin-wall Teflon tube which is housed in a metal jacket plumbed for both cooling water and oven air. The fluid used varies with the mode of operation of the TSAA system. In the check-out and sample modes of operation, cooling water is forced to flow around the walls of the central PTFE tube containing H_2SO_4 in air. The walls of this tube are cooled in a matter of seconds, causing the condensation of H_2SO_4 on its interior walls. However, during the analysis mode, the water is quickly replaced with hot air from the oven, causing the PTFE tube to heat up quickly for the volatilization of H_2SO_4 from its internal walls for transport to the FPD for analysis.

2.2.4 FPD Interface

The FPD interface is the subsystem responsible for integrating the FPD with the downstream side of the collection chamber. It effectively allows the continuous operation of the FPD during all the operation modes of the TSAA system. The components of the FPD interface consist of a pressure surge eliminator (29) and means for two-stream direction control (27) and (28).

During sampling or check-out modes, the stream leaving the collection chamber is directed to point (25) in Figure 3. A large portion of the stream is passed out of the TSAA system via flowmeter (26), flow regulator (27), solenoid valve (28), vacuum pump (53), and activated charcoal bed (11). Approximately 200 cubic centimeters per minute (cc/min) of the stream is directed to the FPD to sustain the hydrogen-fueled flame inside the burner block. During the analysis mode, the entire flow leaving the collection chamber is directed to the FPD for analysis of H_2SO_4.

Immediately upstream from the FPD burner block is a pressure surge eliminator (29). Its function is to minimize pressure fluctuation effects on the flame in the burner block (30) during switching operations of the TSAA system. For example, switching from sample mode to analysis mode will cause a flow change in the collection chamber from about 10 l/min to 0.2 l/min, resulting in relatively high pressure surges occurring in the flame of the FPD. The flame is buffered from such air pressure changes by the inclusion of a pneumatic impedance device (flow regulator) in the plumbing directly downstream of the FPD burner block. This is seen at point (37) in Figure 3.

2.2.5 FPD Assembly

The FPD assembly consists of a burner block (30), photomultiplier tube (31), exhaust gas flow controller (40), hydrogen fuel flow controller (35), vacuum regulator (41), vacuum pump (42), and source of compressed hydrogen fuel (36). The burner block is in the same oven compartment (22) along with the hot transport duct, collection chamber, and FPD interface.

The flow controller (37) for the combustion gases exiting the FPD burner is in a second temperature controlled compartment or oven (39). The purpose of this oven is to flow control the combustion gases originating from the burner block. It also serves to lower the (water) dew point of the combustion gases by introducing a stream of room air into the combustion gas stream. This will prevent water condensation from occurring within the penumatic lines downstream from the flow controller.

A vacuum regulator (41) and pump (42) are connected directly to the flow controller on the lower right side of Figure 3.

The flow control of hydrogen fuel to the burner block is achieved through the utilization of a compressed hydrogen tank (36), pressure regulator (35), flow regulator (34), flowmeter (33), and heat exchanger (32).

By direct flow control of the combustion gases and the hydrogen fuel flow, indirect flow control of the carrier gas entering the burner block is achieved during the analysis mode of operation.

2.2.6 Itineraries of the Streams

In all three modes of operation there are a total of seven streams in the TSAA system. The itinerary of all seven of these streams will be described below in conjunction with Figure 3.

Ambient Samples

An ambient sample will enter solenoid valve (22) and be passed through tee connector (19) where it will be mixed with HCl gas at cross connector (8). It will be passed through hot transport duct (21) and H_2SO_4 collector chamber (23) and be split into two streams at connector tee (25). One path will proceed through pressure surge eliminator (29) and FPD burner block (30) where it will be mixed with ignited hydrogen fuel, resulting in a hydrogen-rich diffusion flame. The combustion gases will pass to flow regulator (37) and the connector (38) where it will be mixed with room air emanating from fixed orifice (40). The mixture will proceed through vacuum regulator (41), vacuum pump (42), and activated charcoal bed (11) where it will be expelled to the ambient air.

Low Level H_2SO_4

Clean and dry air (emanating from the clean/dry air assembly) will pass through solenoid valve (2), pressure regulator (3), and enters the air inlet side of the spray nozzle of the atomizer (9). Dilute H_2SO_4 solution (5) being drawn into the tube (by low pressure created by the high velocity of air flowing over the bottom of the liquid tube) is atomized by a high velocity of dry air. Most of the liquid is impacted on the walls of the holder (6) and is subsequently drained from the assembly via manometer (71). A small portion of the aerosol in the air stream is directed to cross connector (8) where it is mixed with HCl gas. The mixture is transported to the connector (9) where it will be split into two streams. A portion of the stream is transported to hot transport duct (21) where it will continue on in the same fashion as for the ambient sample stream described above. The other portion of the stream is transported through solenoid valve (54) and activated charcoal bed (11) where it is exhausted to the ambient air.

Dilute HCl

Dilute HCl gas is necessarily mixed with sample gas or low level H_2SO_4 emanating from the atomizer.

Clean and dry air (from the clean/dry air assembly) is passed through solenoid valve (12), flow regulator (13), and the low level source of HCl (14), where the air is directed over the surface of the dilute HCl and is passed through solenoid valve (15) to cross connector (8) where it mixes with the sample stream (or the atomizer stream).

Carrier Gas

Carrier gas emanating from the clean/dry air assembly is passed through solenoid valve (16) and the humidifier (18) where it will become saturated with moisture. It will pass through tee connector (19), cross connector (8), tee connector (9), hot transport duct (21), H_2SO_4 collection chamber (23), tee connector (25), pressure surge eliminator (29), and into the FPD burner block (30) where it passes through a hydrogen-rich flame resulting in the chemiluminescence of sulfur (contained in H_2SO_4). From this point, it will proceed on with the combustion gas as was described in 2.2.6.1.

Hydrogen Fuel

Pressurized hydrogen from compressed hydrogen cylinder (36) is passed through pressure regulator (35), flow regulator (34), flowmeter (33), heat exchanger (32), and into the FPD burner block (30) where it will result in a hydrogen-rich flame (consuming the oxygen contained in the air stream). From this point it takes the same path as did the combustion gas stream described in 2.2.6.1.

Collection Chamber Cooling Fluid

During the sampling mode (including check-out), the walls of the collection chamber tube (23) will be cooled by passing cool water around the outside walls of this tube contained inside metal compartment (24). This is accomplished by opening solenoid valve (46) and allowing the water to be passed

through tee connector (44), solenoid valve (43), metal compartment (24), tee connector (48), and solenoid valve (49) to a water drain.

Collection Chamber Heating Fluid

During the analysis mode, the walls of the collection chamber tube (23) are heated by passing hot oven air around the tube. This is accomplished by bringing in hot oven air through solenoid valve (43) and allowing it to purge metal compartment (24) of the liquid water. The mixed-phase fluid is passed from metal compartment (24) through tee connector (48), solenoid valve (50) and into the liquid separator (51). Initially, the water is separated from the stream and is collected in the reservoir portion of the liquid separator. The air stream leaves liquid separator (51) and is passed through cross connector (52), vacuum pump (53), and activated charcoal bed (11) before being exhausted to the atmosphere.

2.2.7 Installation of TSAA System

A block diagram depicting the actual installation of the TSAA system is shown in Figure 6. The system at present is designed for laboratory evaluation and is not a field model instrument. The system is componentized into five compartments. The TSAA system is completely automatic with the sequence of operation modes controlled by a clock timer. However, the system does include provisions for manual control.

2.2.8 Operation Parameters

A complete description of the nominal operational parameters of the TSAA system is presented below:

NOMINAL FPD PARAMETERS

Carrier Gas Flowrate	200 cc/min
Hydrogen Flowrate	200 cc/min
Voltage Setting to Photomultiplier Tube	800 volts DC
Burner Block Temperature	400°F
Flow Controller Temperature	285°F

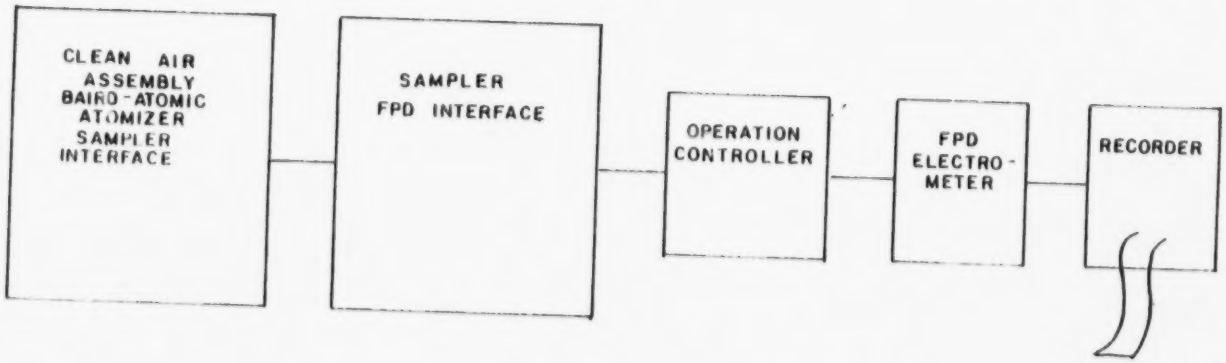

FIGURE 6

BLOCK DIAGRAM OF TSAA SYSTEM INSTALLATION

NOMINAL TSAA SYSTEM PARAMETERS

Upstream pressure during operation B/A atomizer	5 psig
Flow of low level H_2SO_4 from B/A atomizer	20 l/min
Flow of sample gas or low level H_2SO_4 to collection chamber	10 l/min
Sampler oven temperature	400°F
Water Flow through metal jacket	0.25 gal/min
Hot oven air flow through metal jacket	10 l/min
Carrier gas flow to hot transport duct	0.5 l/min
Carrier gas flow through hot transport duct	0.2 l/min

2.3 Evaluation of the TSAA System

The TSAA system was evaluated with respect to determining the overall efficacy of the analytical processes employed in measuring H_2SO_4 levels in air. In addition, the effects of such interferences as SO_2, NH_3, NH_4HSO_4, and $(NH_4)_2SO_4$ were examined. A discussion of the measurement methods employed and the resulting data is presented in the following subsections.

2.3.1 Sampling Efficiency

In order to properly evaluate the sampling efficiency of the collection chamber in the TSAA system, it was decided to compare the TSAA system method with an alternate method of H_2SO_4 collection.

Analysis of Atomizer Output by Alternate Method

The alternate method consists of filtering a stream containing low level H_2SO_4 delivered from the atomizer assembly, using two 47 millimeter glass fiber filters in series. Figure 7 displays a schematic of the apparatus used in sampling H_2SO_4 by the filtration technique.

The apparatus on Figure 7 consists of a Baird-Atomic atomizer assembly (1), all-Teflon filter holder (3) containing two glass fiber filters (4), flowmeter (5), regulator valve (6), and vacuum pump (7). Low level H_2SO_4 in air (artificially produced by the atomizer) was transported to tee connector (2) where the stream was split into two streams. Half of the original stream was transported to the filter holder assembly (3) where it

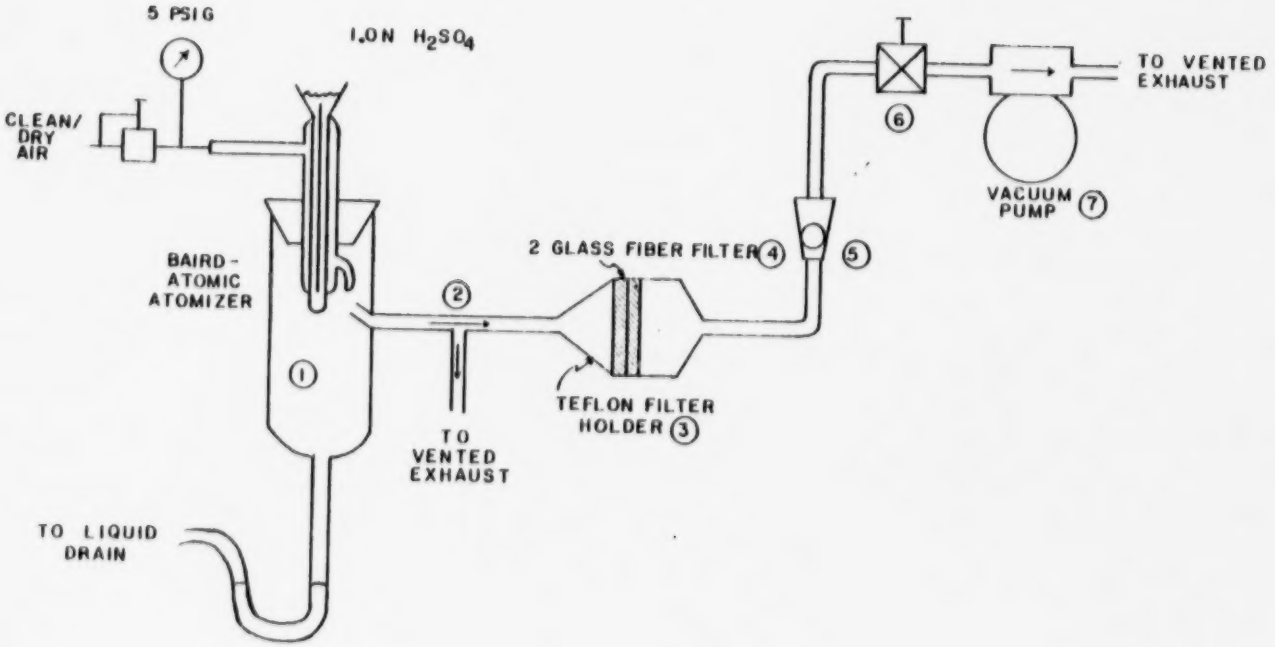

FIGURE 7

APPARATUS OF ALTERNATE SAMPLING METHOD

was forced to pass through <u>two</u> glass fiber filters for the removal of H_2SO_4 mist. Once the stream was transported through the two filters, it was then passed through flowmeter (5), flow regulator (6), and vacuum pump (7). The other half of the original stream was continued on from tee connector (2) to tee connector (8) where it was exhausted to an isolated ventilation system.

The operational parameters of the Baird-Atomic atomizer were identical in this case to those parameters used in testing the TSAA system with the exception of the H_2SO_4 concentration in the feed solution, which was maintained at 1.0 N during periods of alternate sampling. During periods of sampling with the TSAA system, the feed solution was maintained at 0.001 N. This was necessary because of the sensitivity differences (for H_2SO_4) between the alternate analysis method and the TSAA method.

The alternate analysis method employed was the pH determination method. Glass fiber filters exposed to known volumes of air containing low level H_2SO_4 were placed in distilled H_2O and heated to boiling. The solution, upon cooling, was subjected to pH determination using a standardized pH sensor and meter.

Table 2 presents a summary of the data resulting from sampling by the alternate method. A total of six samples and three controls were run exposing the filters to 10 l/min of air delivered from the Baird-Atomic assembly for a total time of 30 minutes. During the test periods, the atomizer was charged with 1 N H_2SO_4 and was operated at an upstream pressure of 5 psig. As determined from Table 2, the average H_2SO_4 concentration in air being delivered to the filter assembly was of the order of 11.1 µg/l. Extrapolating for 0.001 N H_2SO_4 feed solution, the H_2SO_4 concentration in air being delivered from the atomizer assembly would be 11.1 $\mu g/m^3$ for the same upstream pressure setting.

Calibration of FPD Against H_2SO_4

Before the output of the atomizer could be analyzed by the TSAA system, it was necessary to quantify the FPD against known quantities of H_2SO_4. Once this was accomplished the system was able to correlate peak

TABLE 2. ALTERNATE SAMPLING AND ANALYSIS DATA

Sample No.	Make-up of Feed Solution	Volume Air Passed Through Filters (l)	Volume Extraction Solution (ml)	pH	Concentration H_2SO_4 Extraction Solution (moles/liter)
1	1N H_2SO_4	300	50	2.88	659×10^{-6}
2	1N H_2SO_4	300	50	2.70	998×10^{-6}
3	1N H_2SO_4	300	50	2.90	630×10^{-6}
4	1N H_2SO_4	300	50	3.06	435×10^{-6}
5	1N H_2SO_4	300	50	2.86	690×10^{-6}
6	1N H_2SO_4	300	50	2.88	659×10^{-6}
7	Distilled H_2O	300	50	5.54	1.44×10^{-6}
8	Distilled H_2O	300	50	5.86	$.690 \times 10^{-6}$
9	Distilled H_2O	300	50	6.02	$.478 \times 10^{-6}$

Average concentration H_2SO_4 in extraction solution (moles/liter) = 679×10^{-6}

Average concentration H_2SO_4 equivalence in extraction solution (moles/liter) = $.869 \times 10^{-6}$

Corrected moles H_2SO_4 in extraction solution = 678×10^{-6}

Standard deviation of sample no. 1-6 = 181×10^{-6}

Percent standard deviation = 26.7

Average H_2SO_4 concentration in air = 11.1 $\mu g/l$

Equated for normality of .001 = 11.1 $\mu g/M^3$

Source: "Handbook of Chemistry and Physics", Vapor Pressure of Organic Compounds, 47 Edition, Page D122, Chemical Rubber Company.

area quantities of H_2SO_4, thus allowing the actual analysis of the output of the atomizer.

Immediately upon collecting data by the alternate sampling method, the FPD was calibrated against injected quantities of H_2SO_4 via the method displayed in Figure 8. The technique consisted of injecting a quantity of dilute H_2SO_4 in H_2O and volatilizing it in a hot stream of moisture-saturated air. Ambient air was filtered by an activated charcoal and then by a depth type particulate filter. The clean air was bubbled through distilled water to humidify the air to near saturation. The moist air entered an oven and a heat exchanger where it was heated to near 400°F. The hot (moist) air then vaporized the injected H_2SO_4 for transport to the FPD for analysis.

The results of this calibration are displayed in Table 3, and a plot of the data is displayed in Figure 9. The correlation coefficient for the seven data points is .9968, with a slope of 1.95.

Analysis of B/A Output by TSAA System

The final step in the efficiency determination of the TSAA system was to analyze the output of the atomizer at the exact settings that existed during the test conducted with the alternate analysis method. The only exception was that the atomizer would be charged with .001 N H_2SO_4 instead of 1 N H_2SO_4. The pressure upstream from the atomizer was set at 5 psig. The sampling flow rate of the TSAA system was 10 l/min (same as during alternate method sampling). A total of four duplicate tests was conducted, each test differing from the other by the length of sampling period. The data traces for each of the eight tests are included as Appendix A.

At the completion of all the tests, the area (in coulombs) was determined under each peak by Simpson's approximation method. Once each area was determined, the weight (w) of H_2SO_4 representing each area was interpolated from the plot in Figure 9, the FPD calibration against injected quantities of H_2SO_4. From the interpolated H_2SO_4 weight data, the output of H_2SO_4 from the atomizer was determined for the four duplicate test runs. Table 4 presents all the data collected for the eight test runs. The average

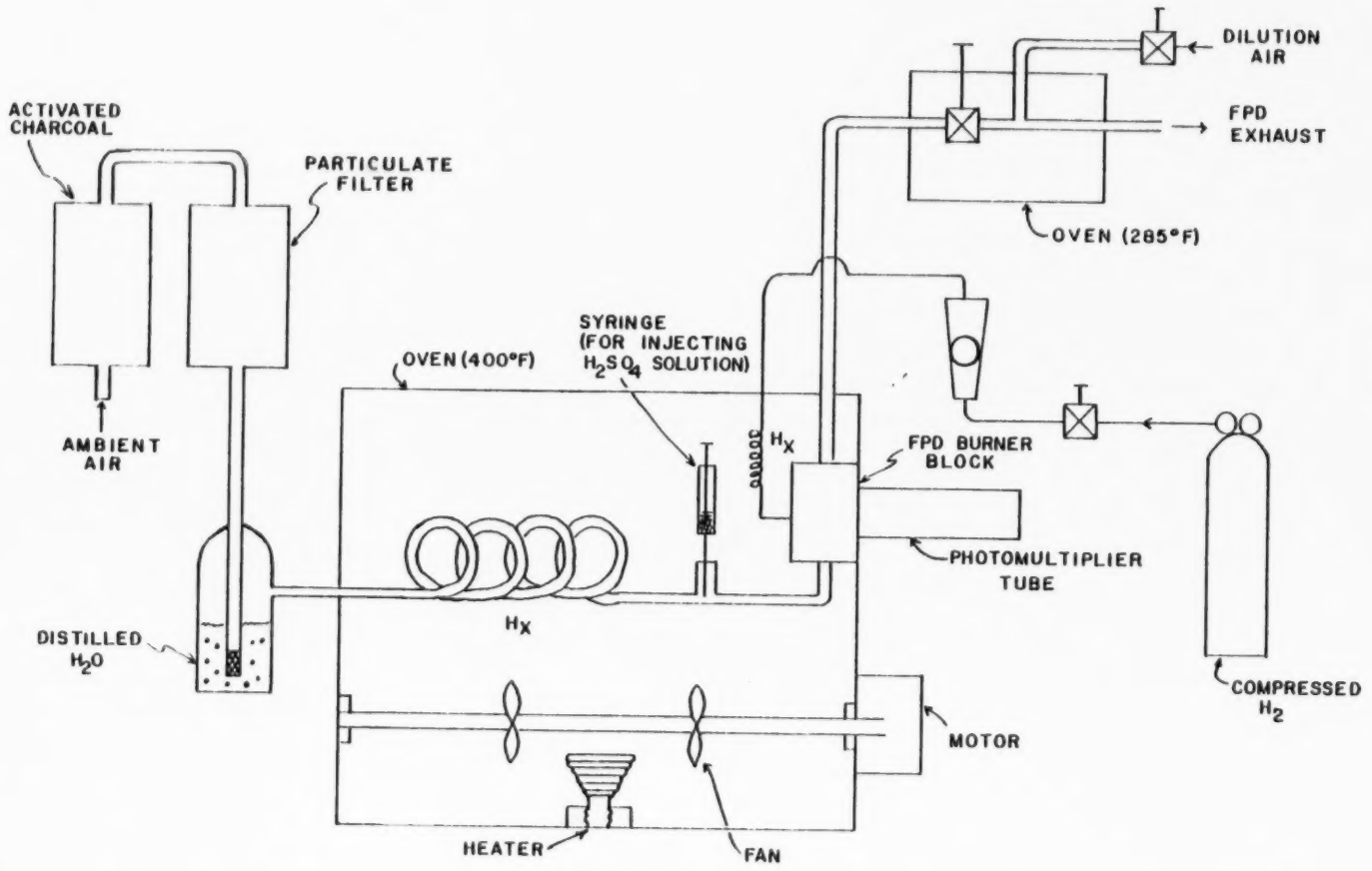

FIGURE 8

CALIBRATION OF THE FPD AGAINST H_2SO_4

TABLE 3. CALIBRATION OF FPD AGAINST H_2SO_4

Sample No.	H_2SO_4 Injected Micrograms (µg)	*Area Under Peak-Coulombs	Log Area	Log (H_2SO_4 Injected)
1	.490	3.99×10^{-5}	-4.399	-.3098
2	.490	4.44×10^{-5}	-4.353	-.3098
3	.368	2.50×10^{-5}	-4.602	-.4342
4	.368	2.28×10^{-5}	-4.642	-.4342
5	.245	1.08×10^{-5}	-4.966	-.6108
6	.245	1.14×10^{-5}	-4.942	-.6108
7	.245	1.04×10^{-5}	-4.982	-.6108

*Simpson's Approximation

Y intercept: -3.774

Slope: 1.95

Correlation Coefficient: .9968

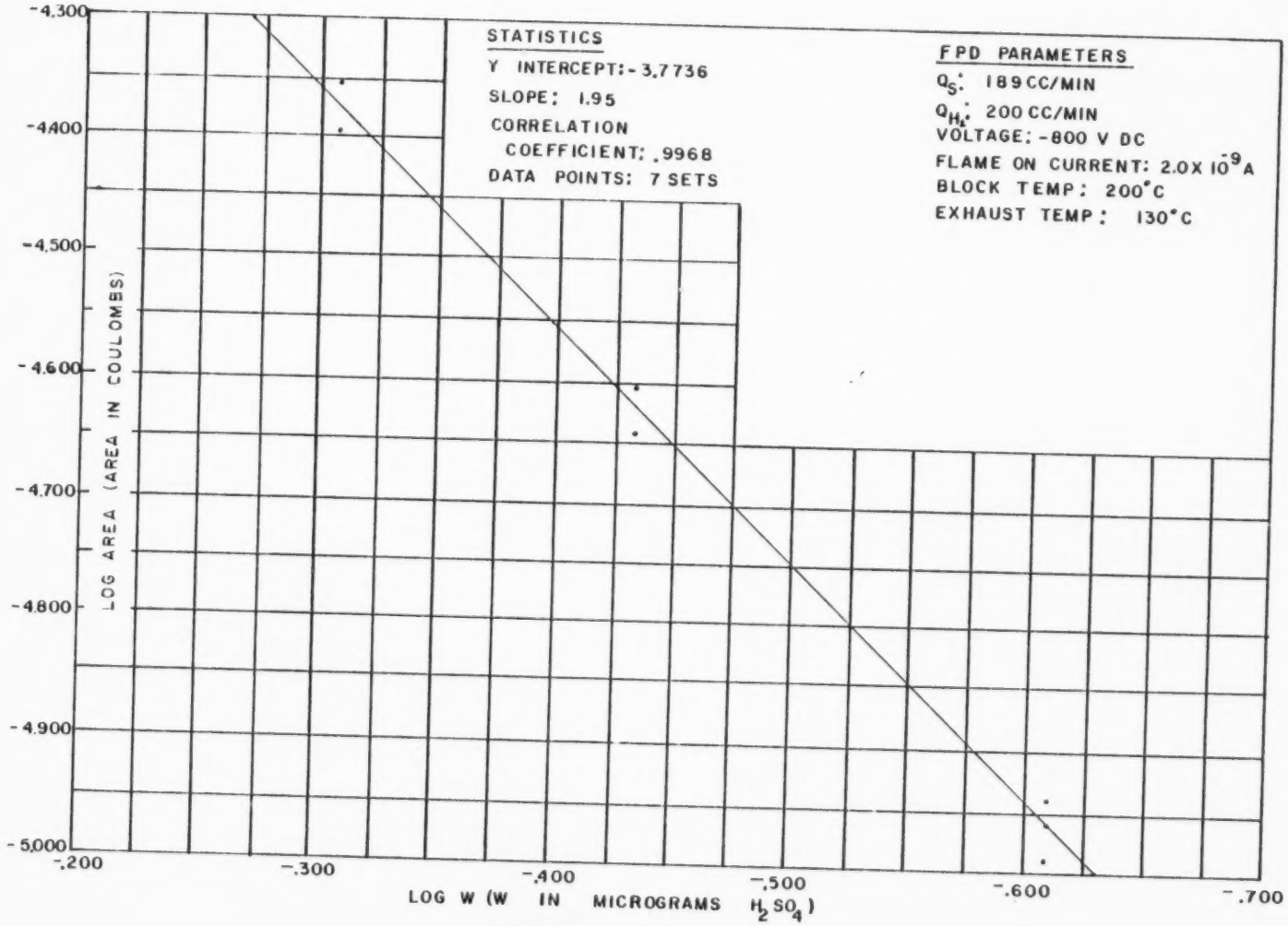

FIGURE 9 INTERNAL VOLATILIZATION OF EXACT QUANTITIES OF H_2SO_4 IN TSAA SYSTEM VS PEAK AREAS

TABLE 4. DATA ON ANALYSIS OF B/A ATOMIZER BY TSAA SYSTEM

Sample No.	Volume Sampled (l)	Peak Area (Coulombs)	Log (area)	Log w*	w (µg)	Conc. H_2SO_4 Output B/A ($\mu g/M^3$)
28	20.9	1.064×10^{-5}	-4.973	-.6162	.242	11.6
27	20.9	1.092×10^{-5}	-4.962	-.6091	.246	11.8
18	26.1	1.683×10^{-5}	-4.774	-.5159	.307	11.8
20	26.1	1.727×10^{-5}	-4.763	-.5072	.311	11.9
30	31.3	2.262×10^{-5}	-4.646	-.4473	.357	11.4
31	31.3	2.532×10^{-5}	-4.597	-.4225	.378	12.1
35	41.7	4.265×10^{-5}	-4.370	-.3063	.494	11.8
36	41.7	4.32×10^{-5}	-4.365	-.3028	.498	11.9

*Interpolated from Figure 9.

$\bar{x} = 11.8$

Average Concentration Output B/A Atomizer: 11.8 $\mu g/M^3$

Standard Deviation: .21 $\mu g/M^3$

% Standard Deviation: 1.8

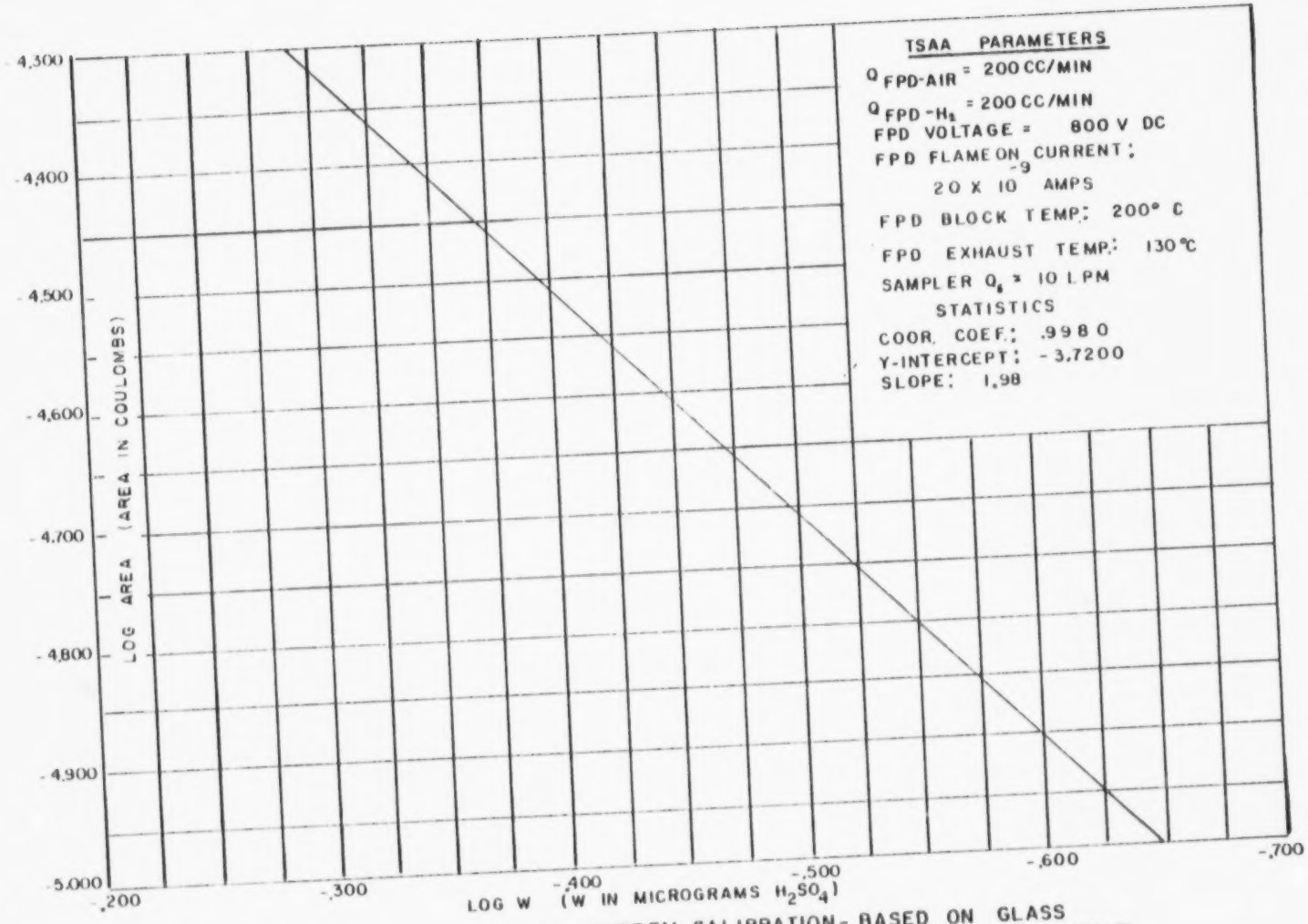

FIGURE 10 TSAA SYSTEM CALIBRATION- BASED ON GLASS FIBER FILTRATION AND pH ANALYSIS OF B/A OUTPUT

concentration of H_2SO_4 delivered by the atomizer was 11.8 $\mu g/m^3$ as interpolated from the FPD calibration curve derived from injected H_2SO_4 (Figure 9). The percent standard deviation for these eight data points was 1.8. An actual plot of the log (area) versus the interpolated log (w) is shown in Figure 10.

Comparison of the Two Analysis Methods

The output of the atomizer operating at .001 N H_2SO_4 at an upstream pressure of 5 psig was determined by the alternate method to be 11.3 $\mu g/m^3$. For the exact same operation conditions, the atomizer output was determined to be 11.8 $\mu g/m^3$ by the TSAA system. Obviously, these results are very close, which indicates at least that the TSAA system is as efficient in its determination of H_2SO_4 in air as the glass filtration technique which has been considered an acceptable technique for sampling H_2SO_4 mist. This comparison is depicted graphically in Figure 11.

2.3.2 Nature of the Data

The data generated by the TSAA system is actually in the form of a chromatogram, in that it displays a plot of signal versus time of elution from the heated collection chamber of any gas phase species having a net response effect on the FPD. This is typically demonstrated in Figures 12 and 13, which are traced copies of actual data generated by the TSAA system in its analysis of a sample stream containing SO_2, HCl, H_2SO_4, and $(NH_4)_2SO_4$. The peaks occurring at 0.1, 1.5, and 2.5 minutes on Figure 12 are the SO_2, HCl, and H_2SO_4, respectively. The separation of H_2SO_4 from $(NH_4)_2SO_4$ is shown on Figure 13. In actuality, the TSAA system separates all those species named above, allowing for the resolution of H_2SO_4.

The quantification of the TSAA system for those species other than H_2SO_4, has not been shown, mainly because of the time constraints of the program. However, in future programs, it may be advisable to investigate the quantitative response of the TSAA system for these other species.

2.3.3 Examination of Potential Interferences

In the course of testing the TSAA system, several of the more obvious potential interferences were introduced into the sample stream in

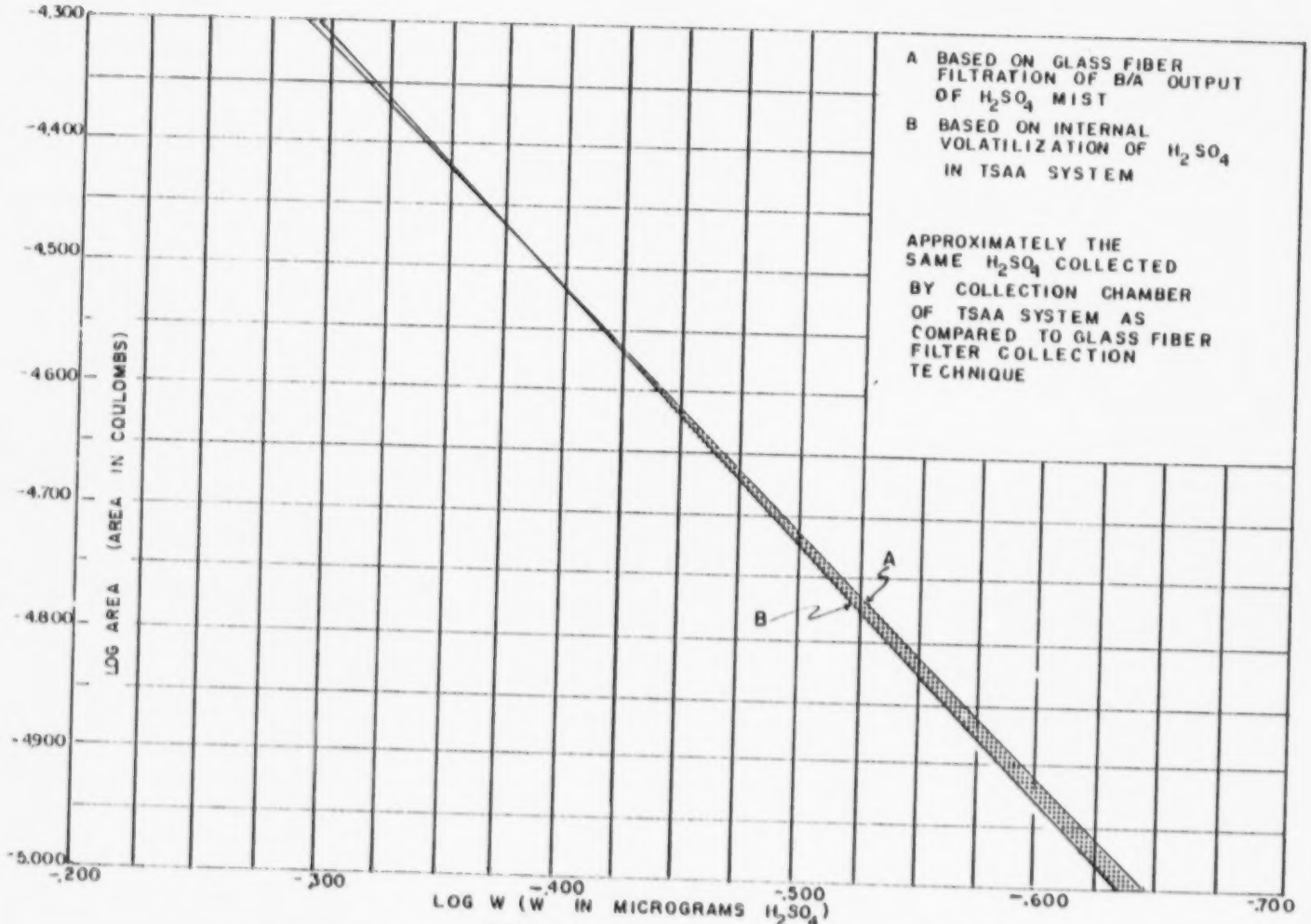

FIGURE 11 COMPARISON IN COLLECTION OF H_2SO_4 SAMPLER IN TSAA SYSTEM VS GLASS FIBER FILTRATION

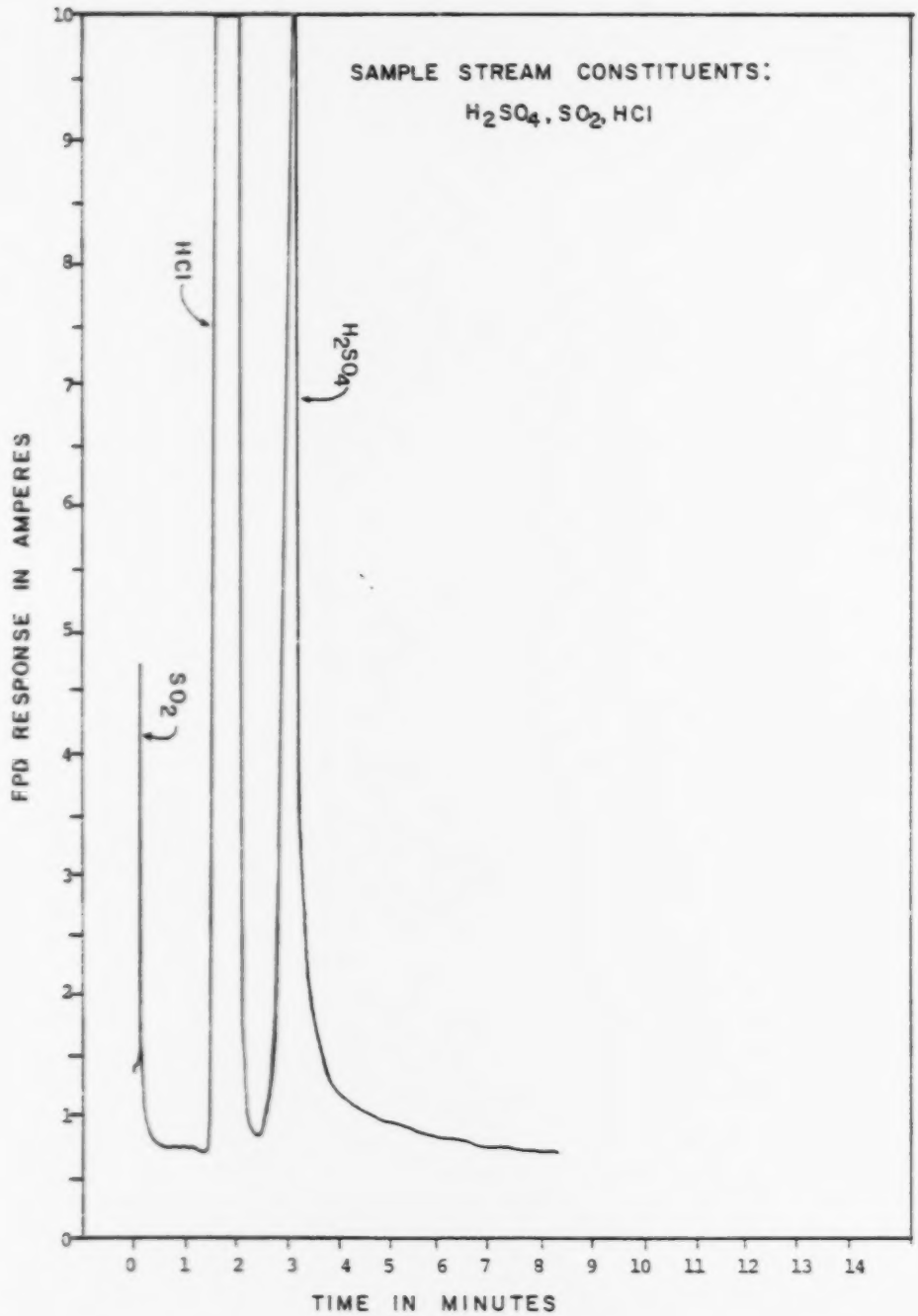

FIGURE 12

DATA IN FORM OF CHROMATOGRAM

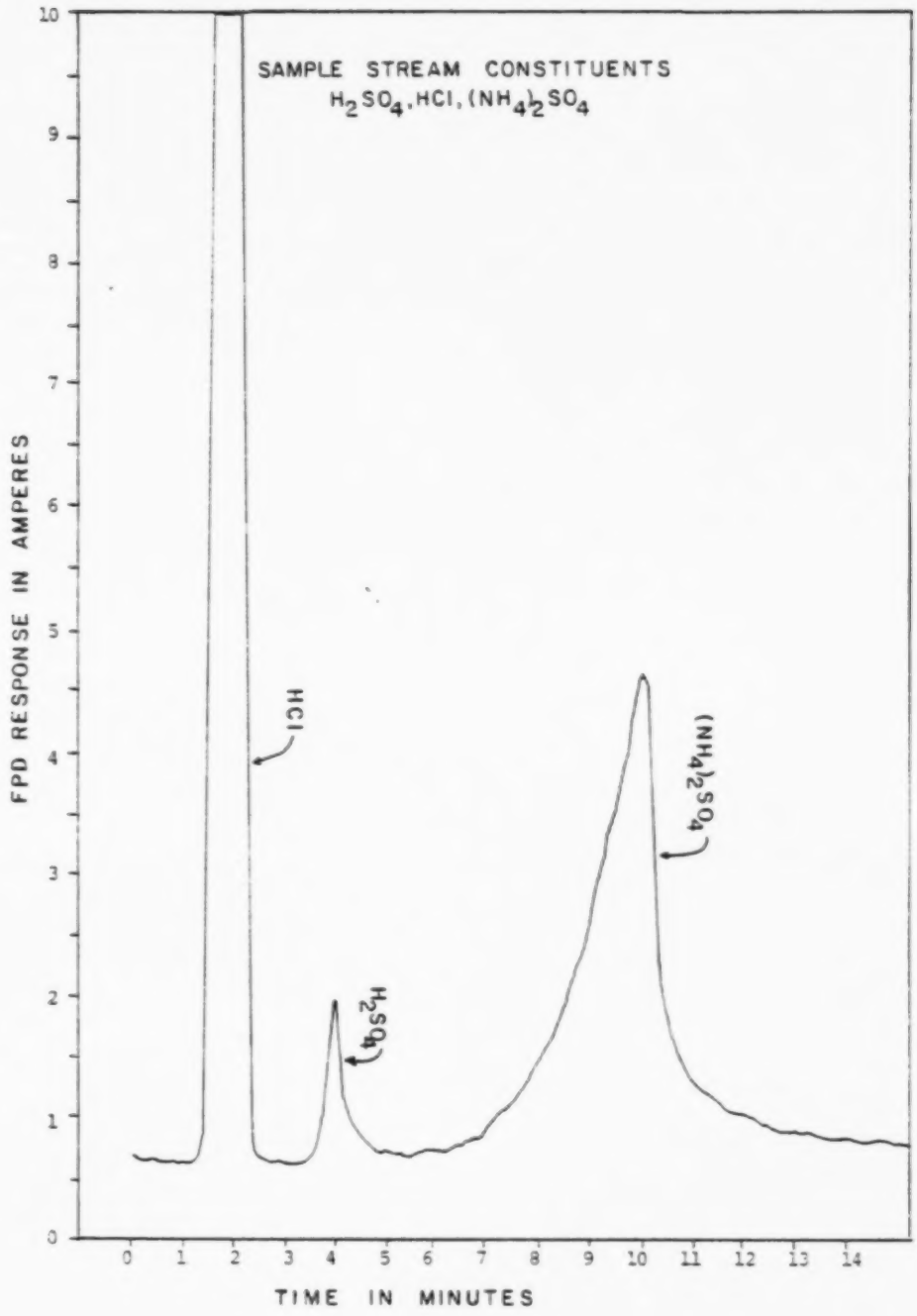

FIGURE 13

DATA IN FORM OF CHROMATOGRAM

an effort to study their effects on the performance of the TSAA system. Of the list of potential interferences, SO_2, NH_4HSO_4, $(NH_4)_2SO_4$, and NH_3 were investigated.

Low levels of SO_2 and NH_3 were introduced separately (or simultaneously) into the sampler interface subsystem of the TSAA system. A pneumatic diagram of the subsystem used is shown in Figure 14.

SO_2 and NH_3 were purchased in Teflon permeation tube form. Nominal emission rates were 282 and 216 ng/min/cm at 25°C for SO_2 and NH_3, respectively. At the operational parameters of the TSAA system, the concentrations of SO_2 and NH_3 in the output stream of the B/A atomizer were of the order of 90 ppb and 52 ppb, respectively.

Results Obtained with SO_2

Two potential adverse effects appear possible from the presence of SO_2; these are interference with H_2SO_4 resolution and addition to the sulfur values attributable to H_2SO_4. However, as shown on Figure 12, resolution of both SO_2 and H_2SO_4 by the TSAA system appears to be acceptable. With respect to the second effect, SO_2 does add significantly to the H_2SO_4 peak (probably by an adsorption-absorption process) as demonstrated by examining the chromatograms in Figures 15 and 16. These figures present chromatograms of two sample streams analyzed by the TSAA system. Both streams contain 10.8 $\mu g/m^3$ H_2SO_4 in air. However, the stream represented by the chromatogram in Figure 15 contains 90 ppb SO_2, as compared to zero SO_2 for Figure 16. Note that the H_2SO_4 peak in Figure 15 is somewhat larger than the peak in Figure 16. The H_2SO_4 peak in Figure 15 can be equated to a 57.7 percent increase in H_2SO_4 concentration, which represents a significant effect by the SO_2.

This additional effect on the H_2SO_4 peak by the SO_2 was virtually eliminated by the introduction of HCl gas into the sample stream. This is demonstrated by examining the three chromatograms displayed in Figures 17, 18, and 19. The H_2SO_4 concentration was identical for all three sample streams; however, the stream chromatographed in Figures 17 and 19 contained dilute HCl gas whereas the stream in Figures 18 and 19 contained 90 ppb SO_2 gas.

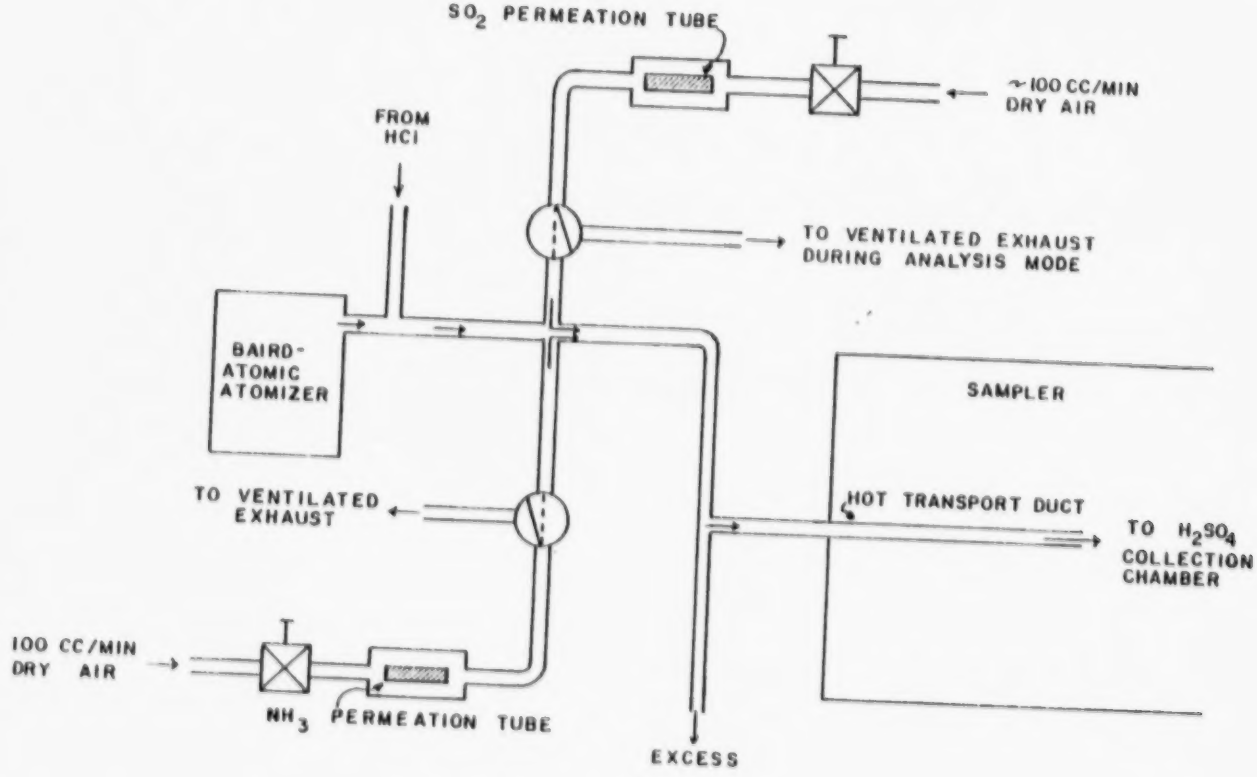

FIGURE 14

PNEUMATIC DIAGRAM OF SYSTEM FOR THE INTRODUCTION SO_2 & NH_3 INTO TSAA SYSTEM

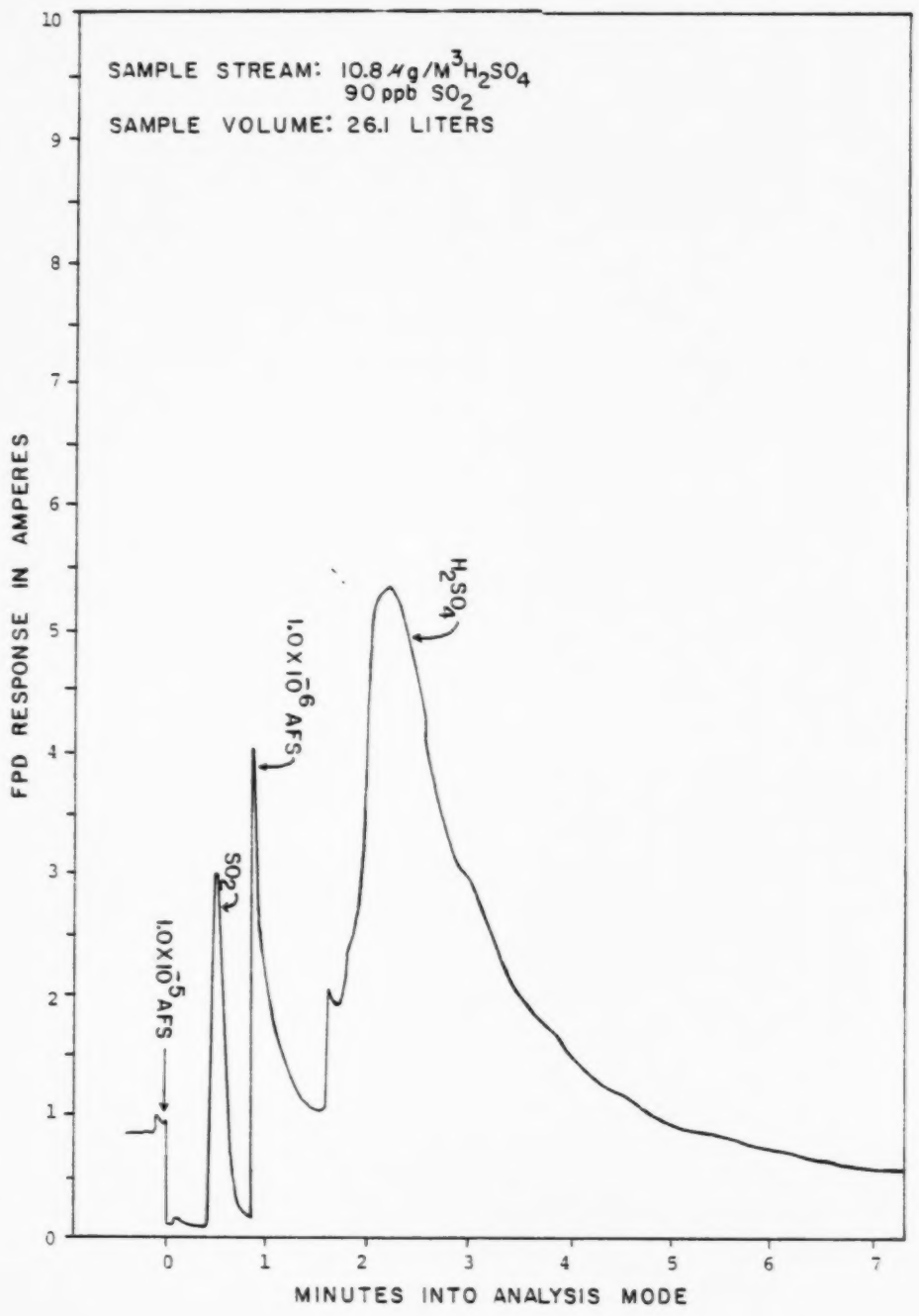

FIGURE 15

SO_2 EFFECT ON TSAA SYSTEM

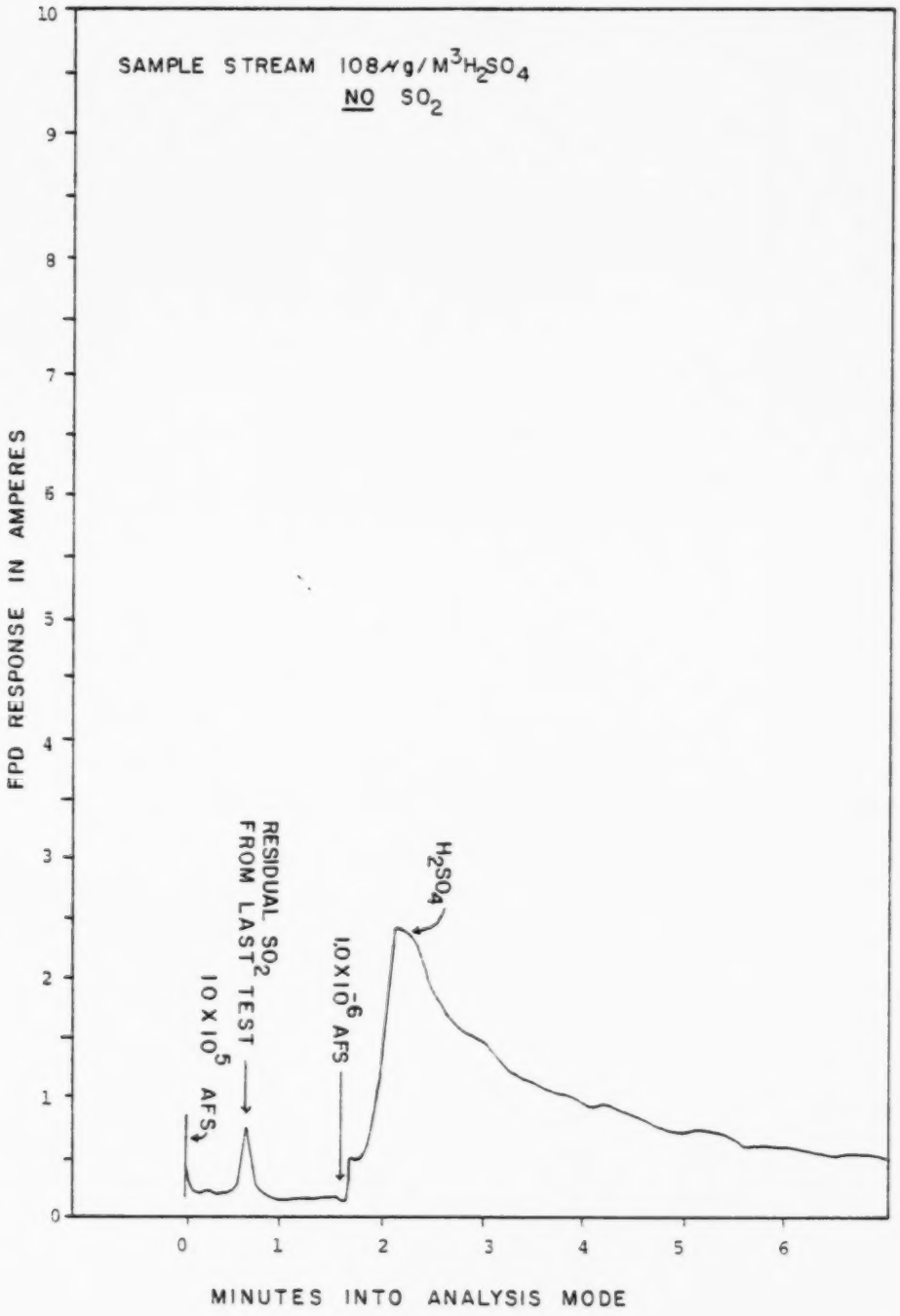

FIGURE 16

SO_2 EFFECT ON TSAA SYSTEM

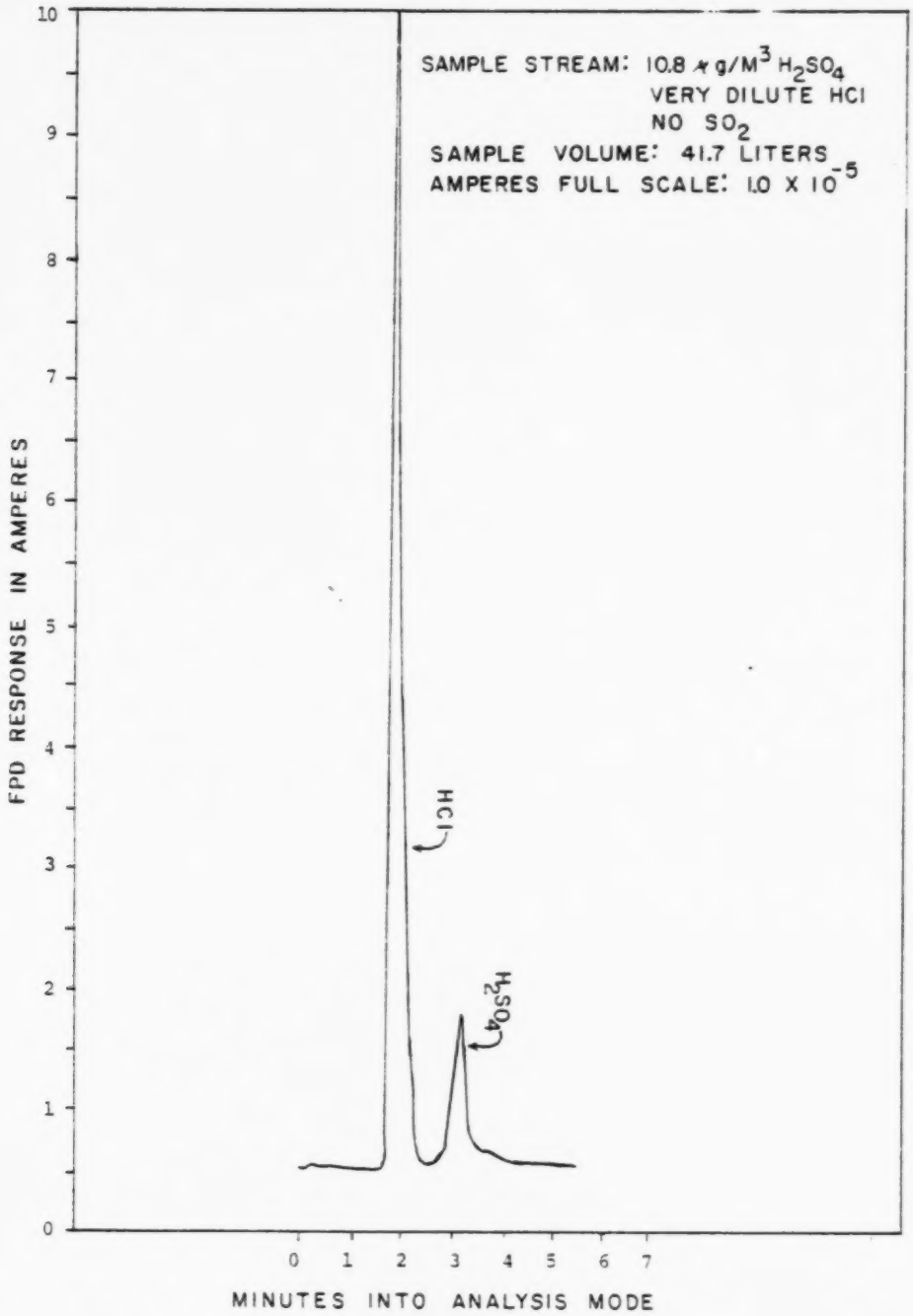
SAMPLE STREAM: 10.8 μg/M³ H_2SO_4
VERY DILUTE HCl
NO SO_2
SAMPLE VOLUME: 41.7 LITERS
AMPERES FULL SCALE: 1.0 X 10^{-5}
FPD RESPONSE IN AMPERES
MINUTES INTO ANALYSIS MODE
HCl
H_2SO_4
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7

FIGURE 17

ELIMINATION OF SO_2 INTERFERENCE

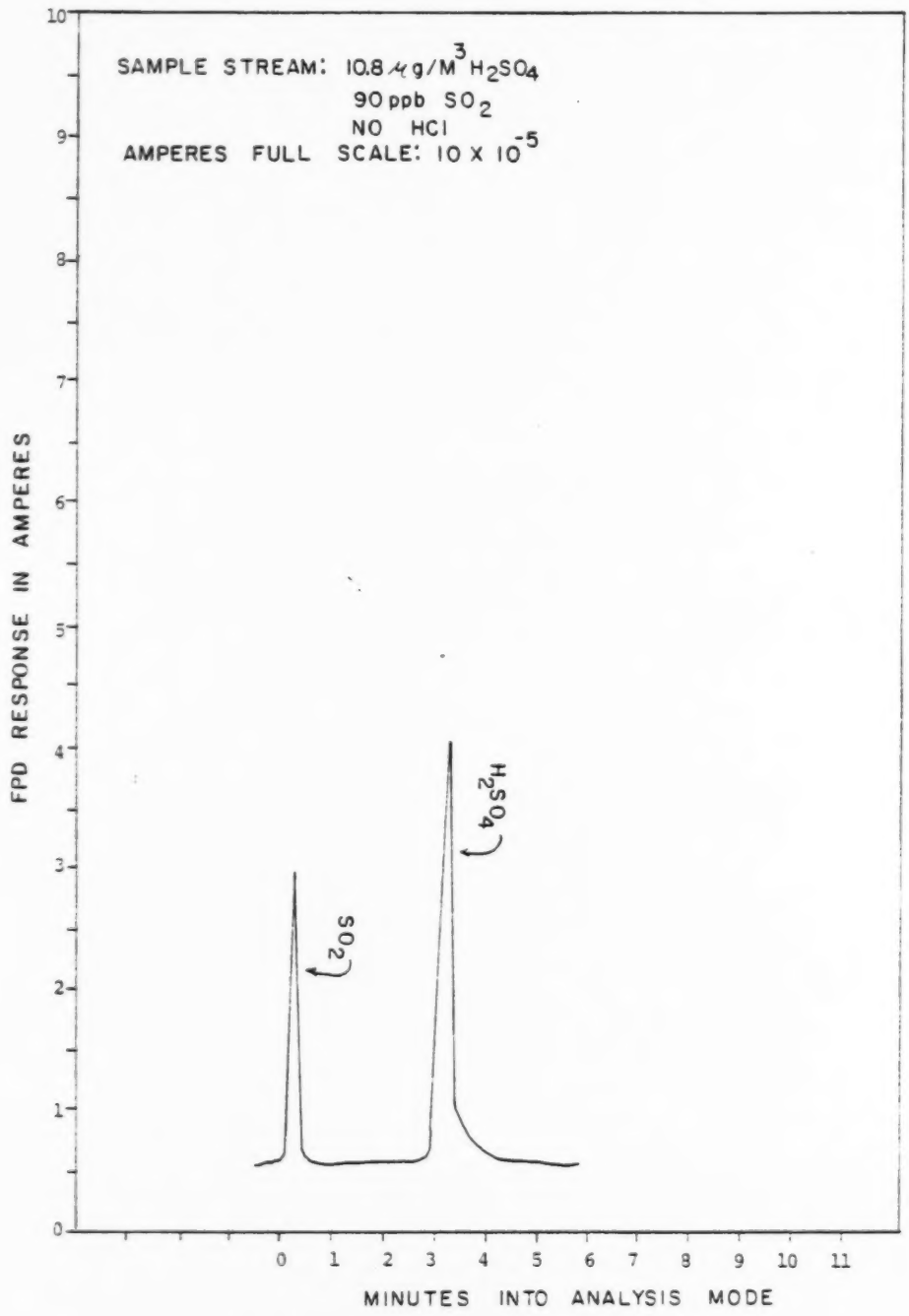

FIGURE 18

ELIMINATION OF SO_2 INTERFERENCE

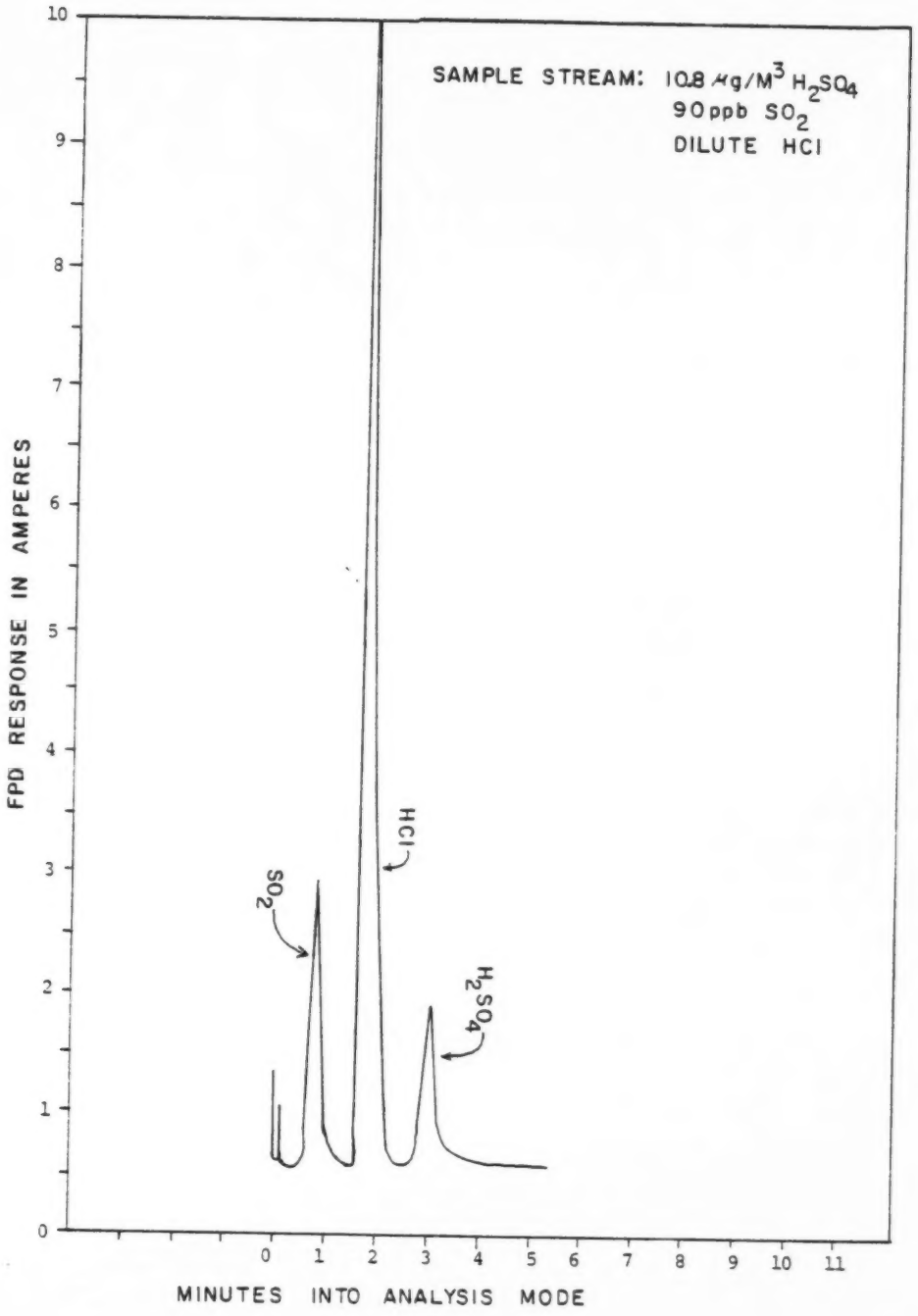

FIGURE 19

ELIMINATION OF SO_2 INTERFERENCE

Note that, in Figure 18, the presence of HCl gas completely eliminated the SO_2 effect on the H_2SO_4 peak demonstrated in Figure 17.

Results Obtained with NH_3

The NH_3 effect on H_2SO_4 analysis is very much different from that of SO_2 effect; however, NH_3 does significantly interfere with the H_2SO_4 analysis. The presence of NH_3 (in a sample stream containing H_2SO_4) appears to convert a significant fraction of the collected H_2SO_4 to $(NH_4)_2SO_4$. This is demonstrated in Figure 20, where more than 50 percent of the H_2SO_4 was converted to $(NH_4)_2SO_4$ by ammonia in the sample. The chromatogram of the NH_3 doped stream indicates an almost total conversion of H_2SO_4 to $(NH_4)_2SO_4$. The levels of NH_3 and H_2SO_4 were 52 ppb and 10.8 $\mu g/m^3$, respectively, and the sample volume was 31.3 liters.

However, it should be pointed out that, as in the case of the SO_2-doped sample stream, the presence of HCl gas with NH_3 and H_2SO_4 in the same stream appeared to eliminate the NH_3 interference. This observation is demonstrated by comparison of Figure 20 with Figure 21, which present chromatograms of two identical streams with respect to NH_3 and H_2SO_4 levels. The difference is that one stream contained HCl gas (Figure 21) and the other stream was free of HCl gas (Figure 20).

Results Obtained with NH_4HSO_4 and $(NH_4)_2SO_4$

The potential for interference of NH_4HSO_4 and $(NH_4)_2SO_4$ in the analysis of H_2SO_4 was of great concern to the validity of the TSAA sampler. Like H_2SO_4, these ammonium salts contain sulfur (thereby being easily detected by the FPD) and also exist in the atmosphere in particulate form. Our original impression was that, if the TSAA system did remove these ammoniated salts from the sample stream, the FPD would falsely detect H_2SO_4. This concern has been greatly minimized by virtue of utilizing a collection mechanism for H_2SO_4 which does not perform media filtration. Because the ammoniated salts exist in crystalline form and possess relatively high boiling points, it is believed

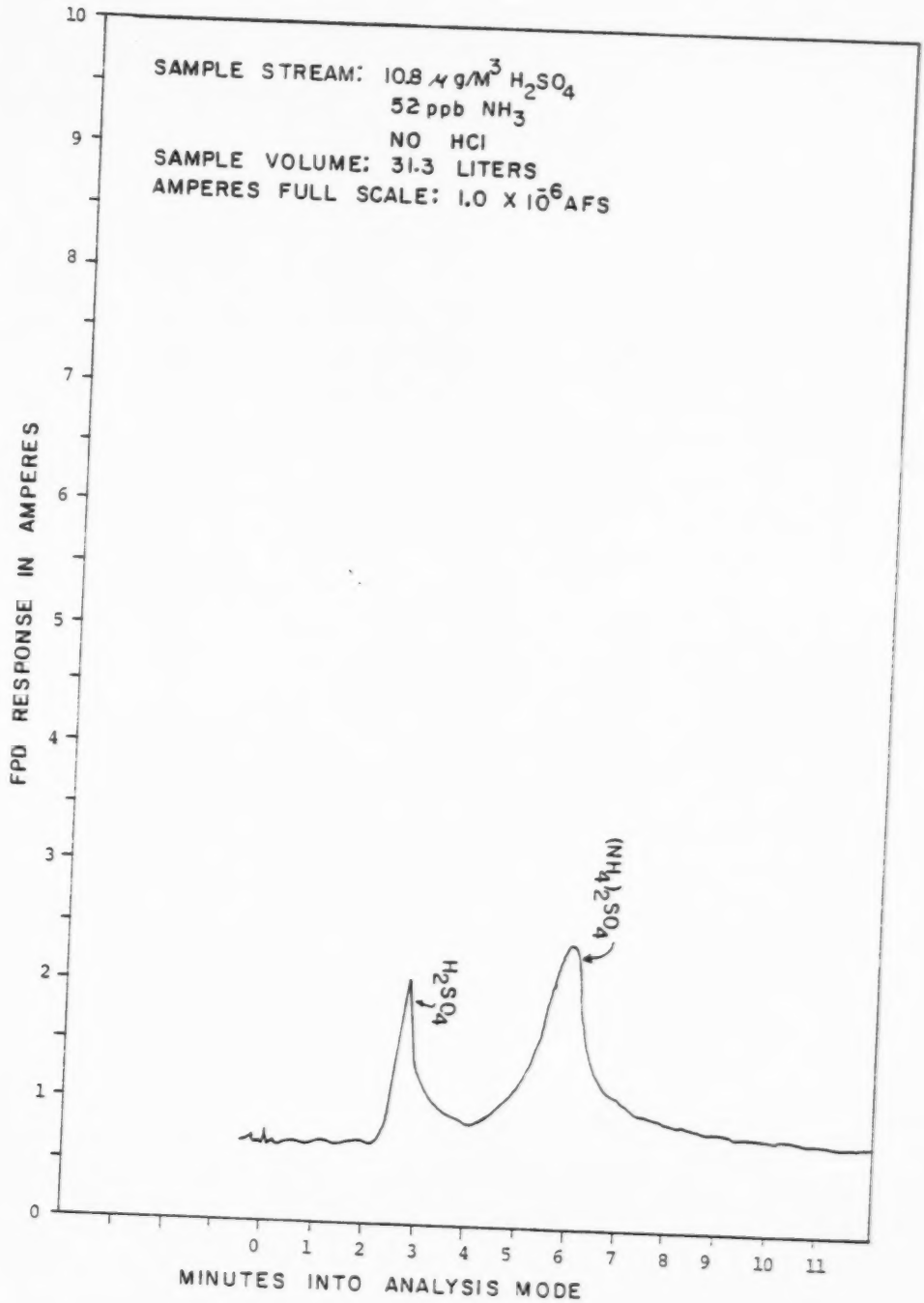

FIGURE 20

ELIMINATION OF NH_3 INTERFERENCE

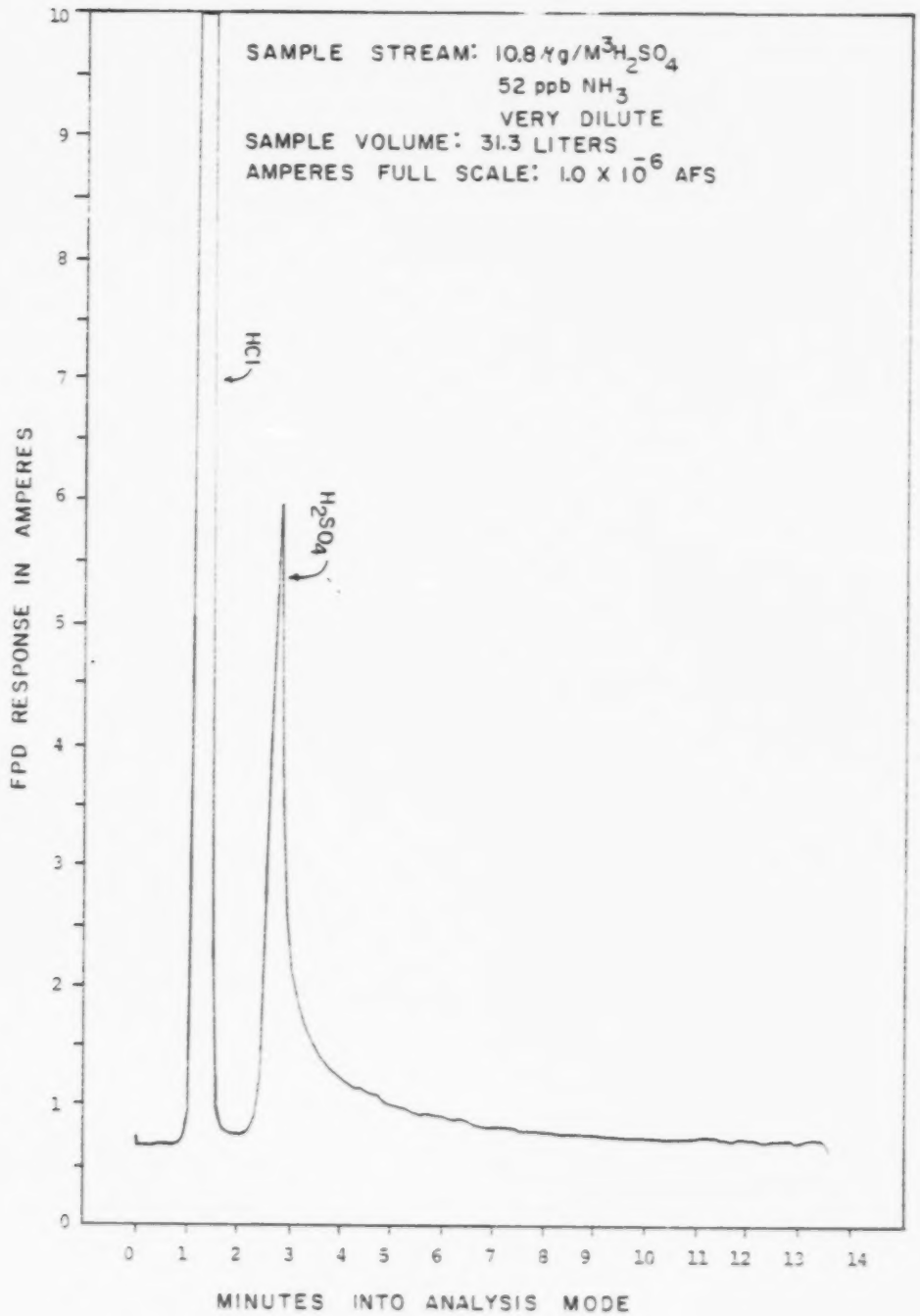

FIGURE 21

ELIMINATION OF NH_3 INTERFERENCE

that they will exhibit the properties of a solid particulate throughout the hot transport duct and collection chamber and will not be condensed or collected by the collection chamber.

Perhaps the most important reason for discounting ammonium salt interference is that the TSAA system (during analysis mode) accomplishes fractional separation of H_2SO_4 from the ammonium salts, thus resolving H_2SO_4 from these potential interferences. This observation was pointed out in Section 2.3.2.

2.3.4 Comparison of FPD Response Characteristics to H_2SO_4 and SO_2

A comparison was made between the response characteristics of the FPD to SO_2 and H_2SO_4. The FPD was calibrated against SO_2 (on a real time basis) and H_2SO_4 (on an injection-volatilization basis). An SO_2 curve was generated, as shown in Figure 22, by plotting SO_2 concentration against net response. Likewise, an H_2SO_4 curve (Figure 9) was generated by plotting weight (w) of H_2SO_4 injected against resulting area under the peaks. Because the SO_2 curve is a continuous response for a constant SO_2 concentration over an infinite time, the SO_2 curve was normalized to the H_2SO_4 curve. This was accomplished by transforming the H_2SO_4 triangular shaped peaks to rectangular shaped peaks and computing the FPD response. This computation for each data point is as follows:

Referring to H_2SO_4 curve,

$A_i = R \times t$ (transformed from triangular shaped to rectangular shaped peaks)

$\log A_i = \log (R_i \times t_i)$

$\log A_i = \log R_i t \log t_i$

$\log R_i = \log A_i - \log t_i$.

Referring to SO_2 curve,

R_i equivalent to C_{SO_2} (ppm SO_2)

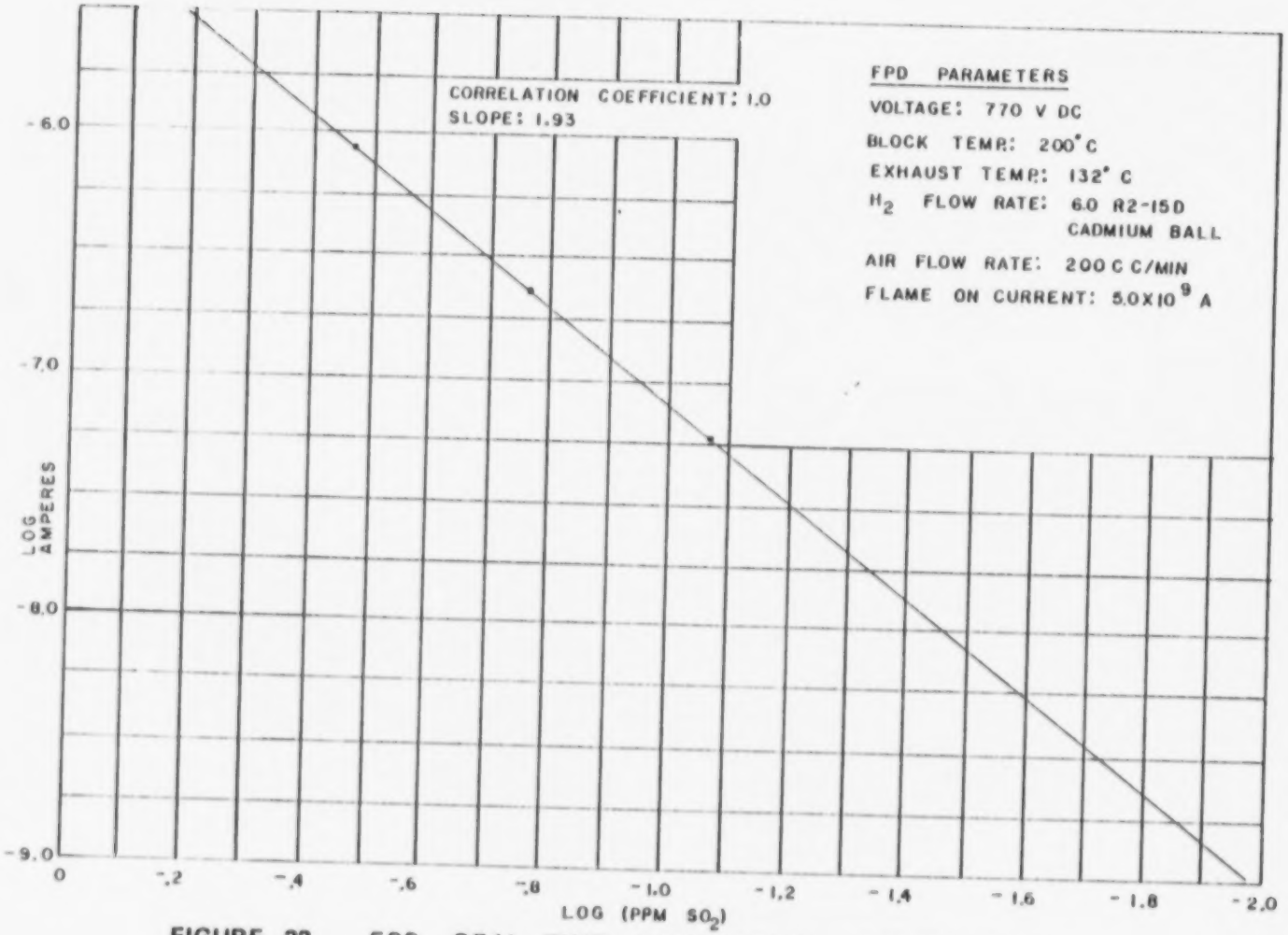

FIGURE 22 FPD REAL TIME CALIBRATION AGAINST SO_2

$$C_{SO_2} = C_s$$

$$C_s' = \frac{32}{24.5} C_s$$

$$W_s = C_s' \times Q_{FPD} \times t_i.$$

Where A_i = Area under curve for i injection of H_2SO_4 (coulombs or ampere seconds),

t_i = time under curve for i injection

R_i = net response in amperes

C_{SO_2} = ppm SO_2 in air

C_S = ppm S in air

C_S' = micrograms/liter of air

Q_{FPD} = sample flowrate into FPD in liters/minute

W_s = weight of sulfur in micrograms.

Figure 23 displays a comparison of H_2SO_4 and SO_2 (normalized) curves with the abscissa being units of weight (w) of equivalent injected sulfur and the ordinate being area under the curve (in coulombs).

Note that the curves are close at the lower end of the curve but diverge at the higher end. For example, the curves cross at an area of 1.19×10^{-5} coulombs. However, at an area of 3.98×10^{-5} coulombs, the curves diverge to require 13.7% more sulfur derived from H_2SO_4 to yield the same area for sulfur derived from SO_2.

These results are not necessarily conclusive in comparing FPD response characteristics; however, the data may indicate that the FPD flame is not as efficient in the production of energized species of sulfur (S*) from H_2SO_4 as compared to producing S* species from SO_2. This conclusion appears logical, but to date has not been definitely proven.

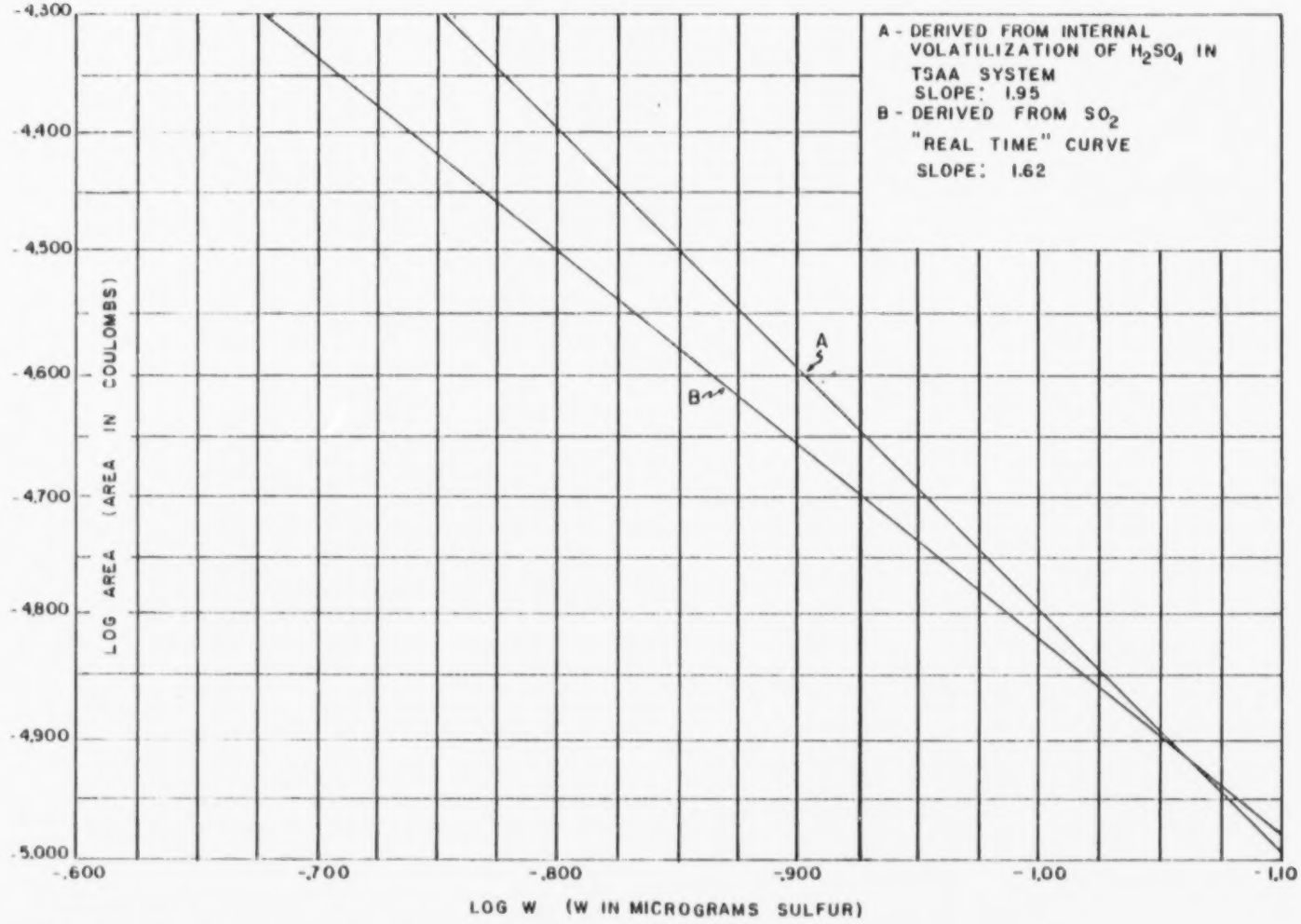

FIGURE 23 COMPARISON OF RESPONSE CHARACTERISTICS BETWEEN H_2SO_4 AND SO_2

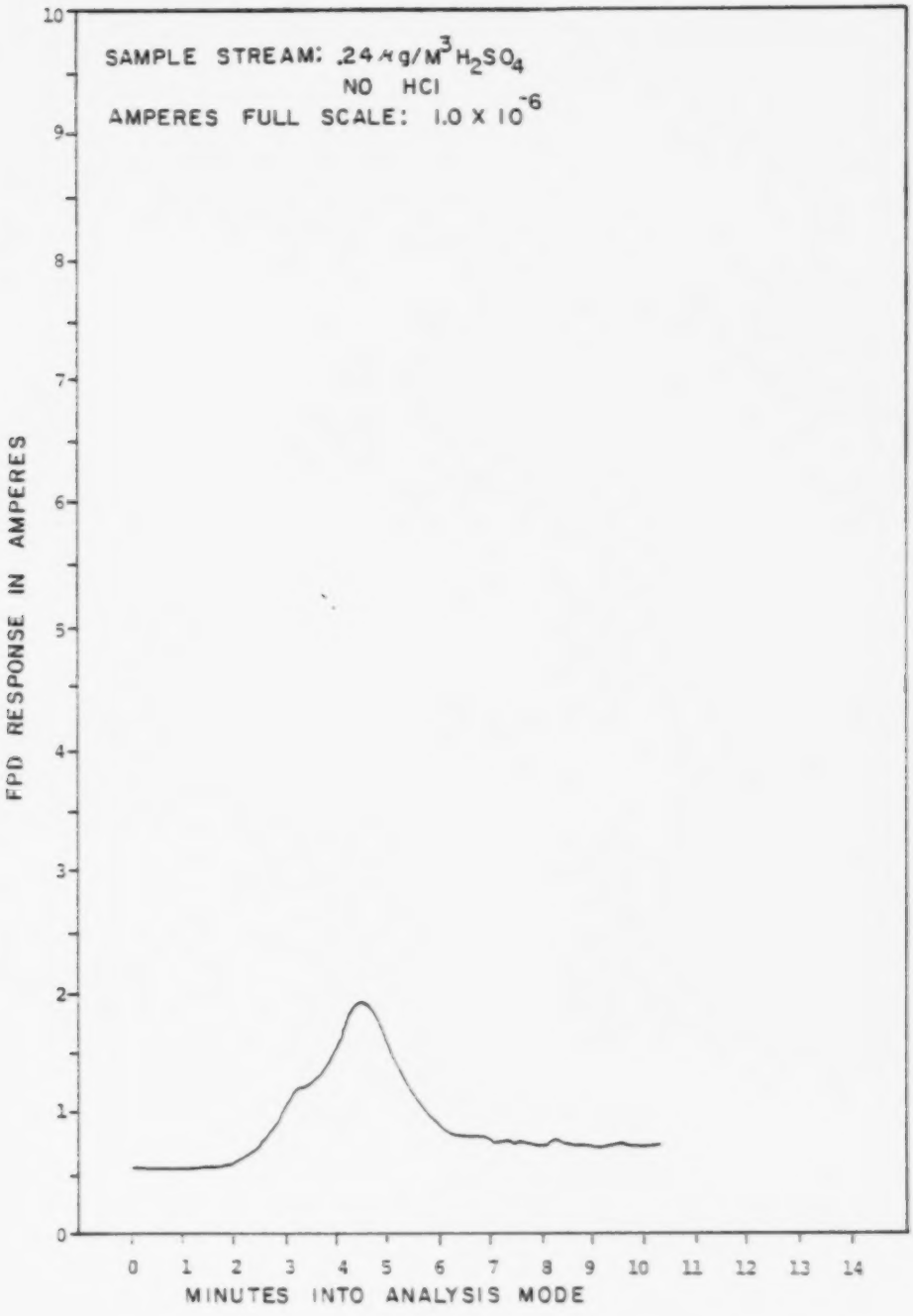

FIGURE 24

TSAA SYSTEM SENSITIVITY

In future studies of this nature, it would be of interest to compare the FPD response characteristics to SO_2 and H_2SO_4 on a continuous (real time) basis, thus eliminating the time (t_i) parameter in generating area data.

2.3.5 TSAA System Sensitivity to H_2SO_4

The TSAA system was challenged with a level of 0.24 $\mu g/m^3$ H_2SO_4 in air. Figure 24 displays a copy of the actual chromatogram of the analysis. The atomizer was allowed to atomize 160 milliliters of 0.00002 normal H_2SO_4 in H_2O for a period of 83.5 minutes. During this period, the TSAA system sampled the output of the atomizer at a flowrate of 10 liters per minute or 835 liters of low level H_2SO_4 in air. The area of the resulting peak was 8.56×10^{-6} coulombs which reflected a mass of 0.22 micrograms H_2SO_4, referring back to the curve depicted in Figure 9.

The nominal H_2SO_4 delivered, based on an extrapolation for 0.00002 normal H_2SO_4 from 0.001 normal H_2SO_4 (and a sample volume of 835 liters), was 0.26 $\mu g/m^3$.

Observe that the actual peak is irregular in shape and later than usual, which may have resulted from the presence of a small amount of NH_3 present in the clean air supply to the atomizer. The peak may have been more symmetrical and earlier if HCl had been introduced into the output stream of the atomizer during the sampling period.

Note also that the maximum FPD response during the analysis mode was of the order of 1.5×10^{-7} amperes. This response is relatively high for an FPD, which can easily monitor total sulfur response of the order of 1.0×10^{-9} amperes, approximately ¼ the concentration of H_2SO_4 (or .06 $\mu g/m^3$) produced during the above test. Achieving optimum system performance may require detailed study of the evaporation characteristics of H_2SO_4 during volatilization from the collection chamber.

APPENDIX A

TRACES OF FPD RESPONSE IN TSAA CALIBRATION TEST SERIES
(CORRESPONDS TO DATA ON TABLE 4 OF REPORT)

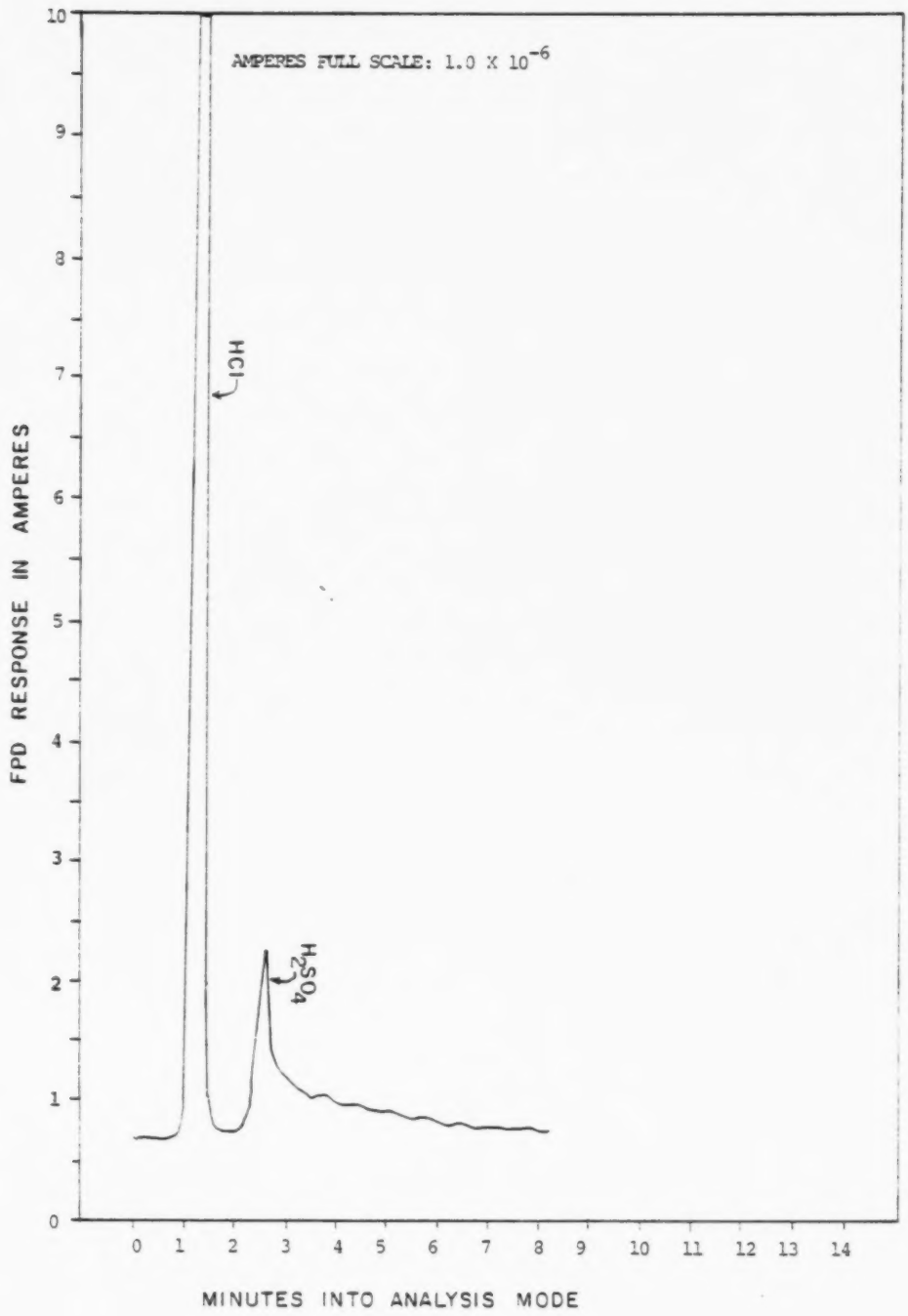
AMPERES FULL SCALE: 1.0 X 10^{-6}
FPD RESPONSE IN AMPERES
HCl
H_2SO_4
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
MINUTES INTO ANALYSIS MODE

FIGURE A-1

COPY OF RAW DATA FOR SAMPLE NO. 28

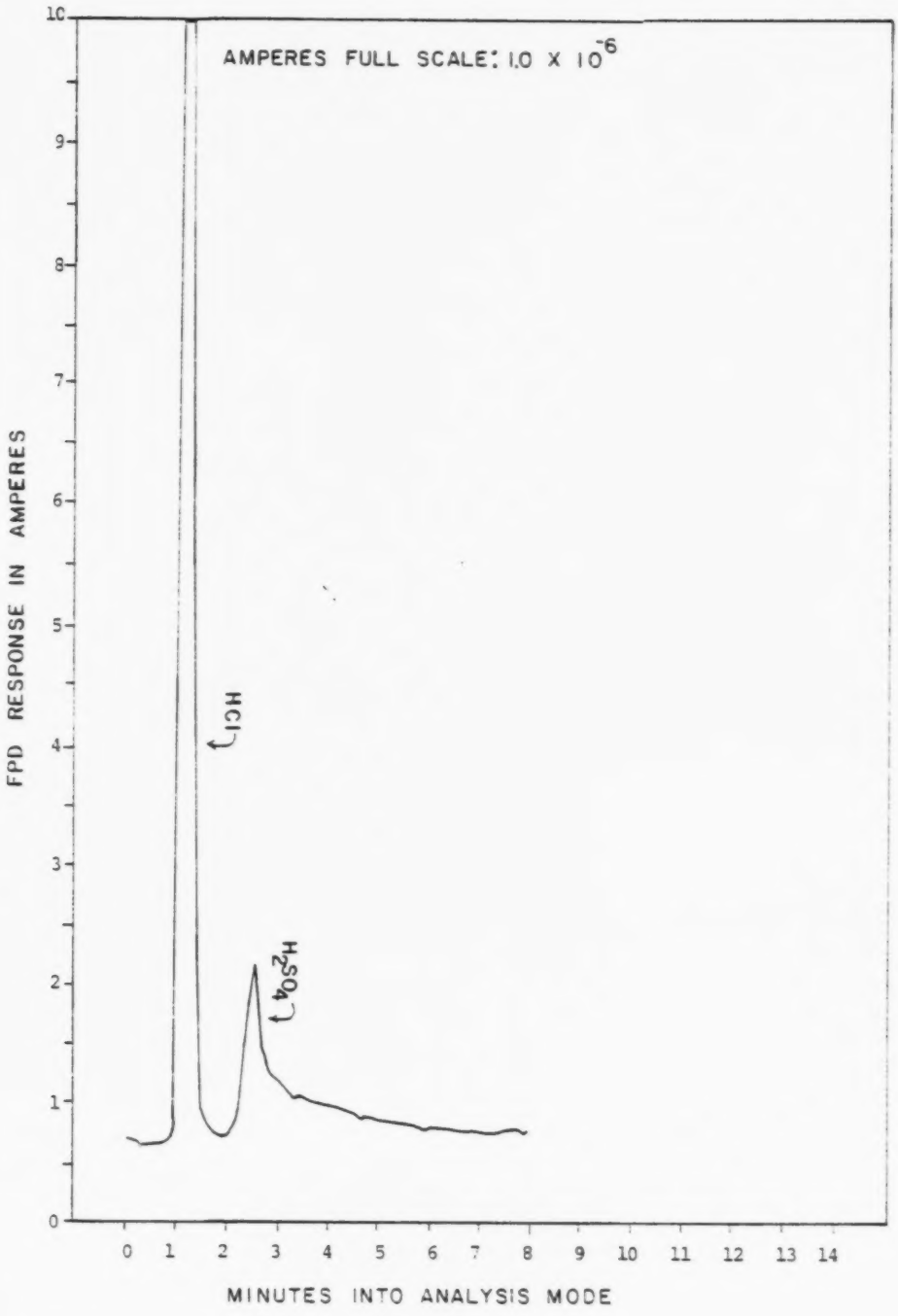

FIGURE A-2

COPY OF RAW DATA FOR SAMPLE NO. 27

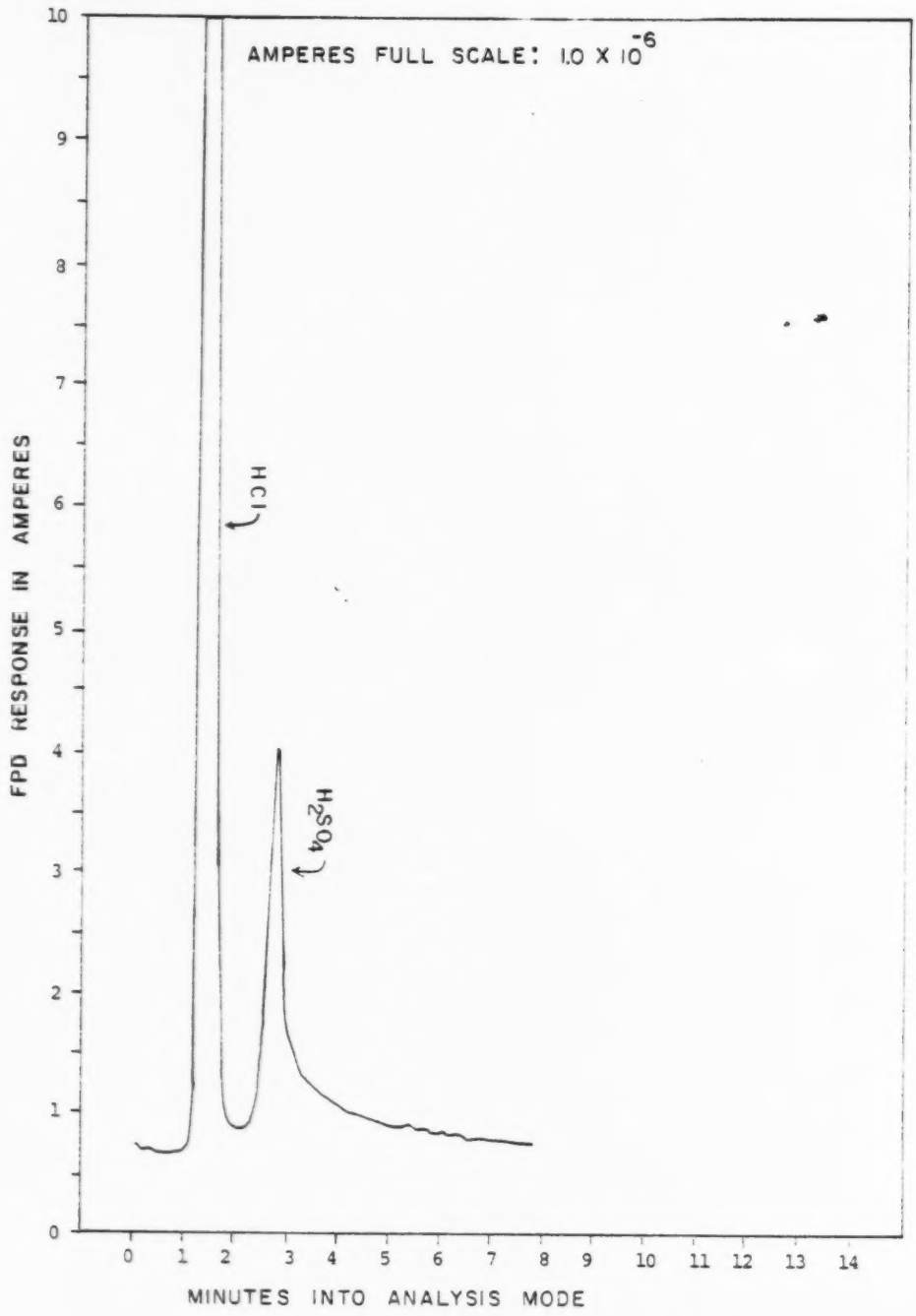

FIGURE A-3

COPY OF RAW DATA FOR SAMPLE NO. 18

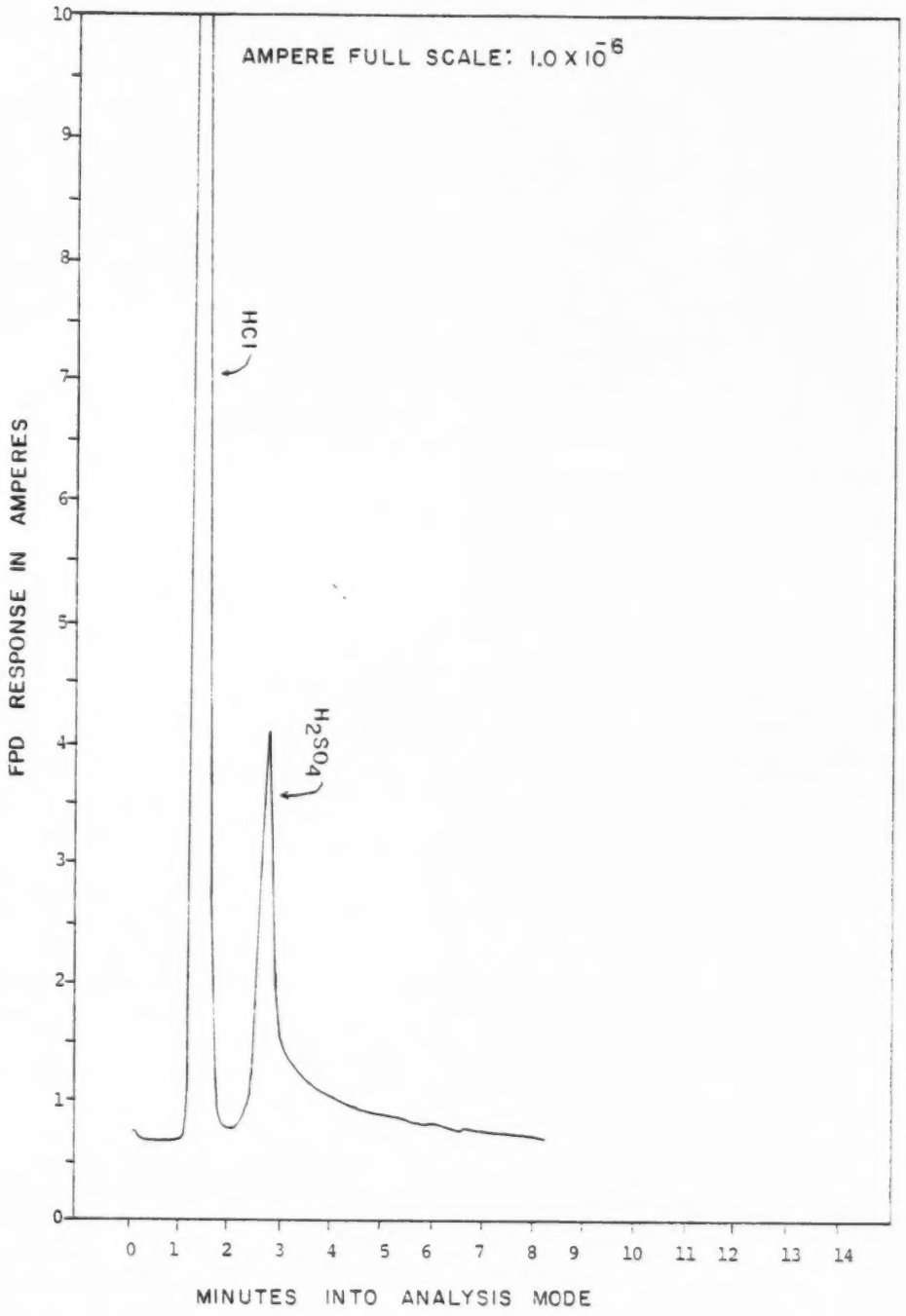
AMPERE FULL SCALE: 1.0×10^{-6}
FPD RESPONSE IN AMPERES
HCl
H_2SO_4
0 1 2 3 4 5 6 7 8 9 10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
MINUTES INTO ANALYSIS MODE

FIGURE A-4

COPY OF RAW DATA FOR SAMPLE NO. 20

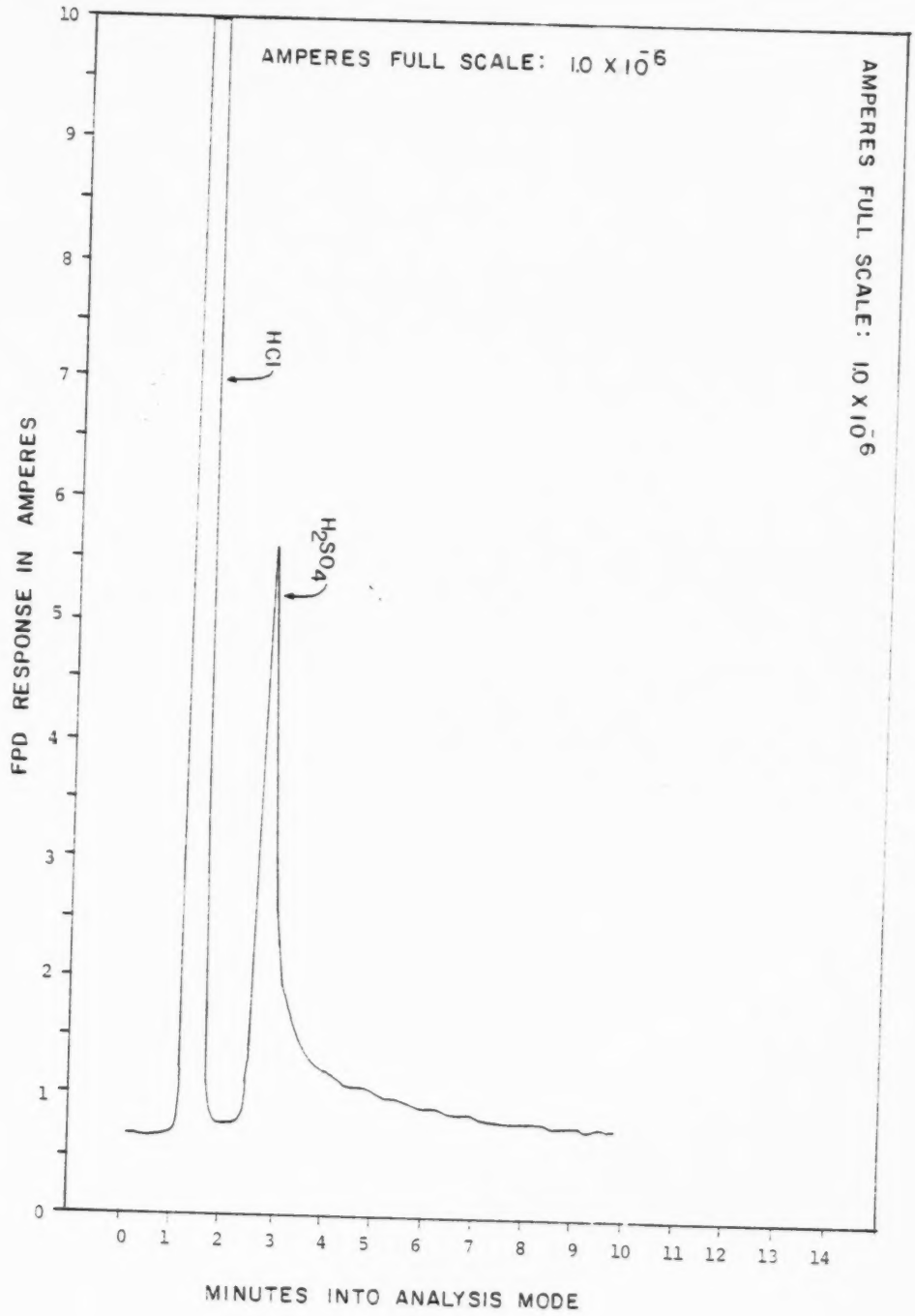

FIGURE A-5

COPY OF RAW DATA FOR SAMPLE NO. 30

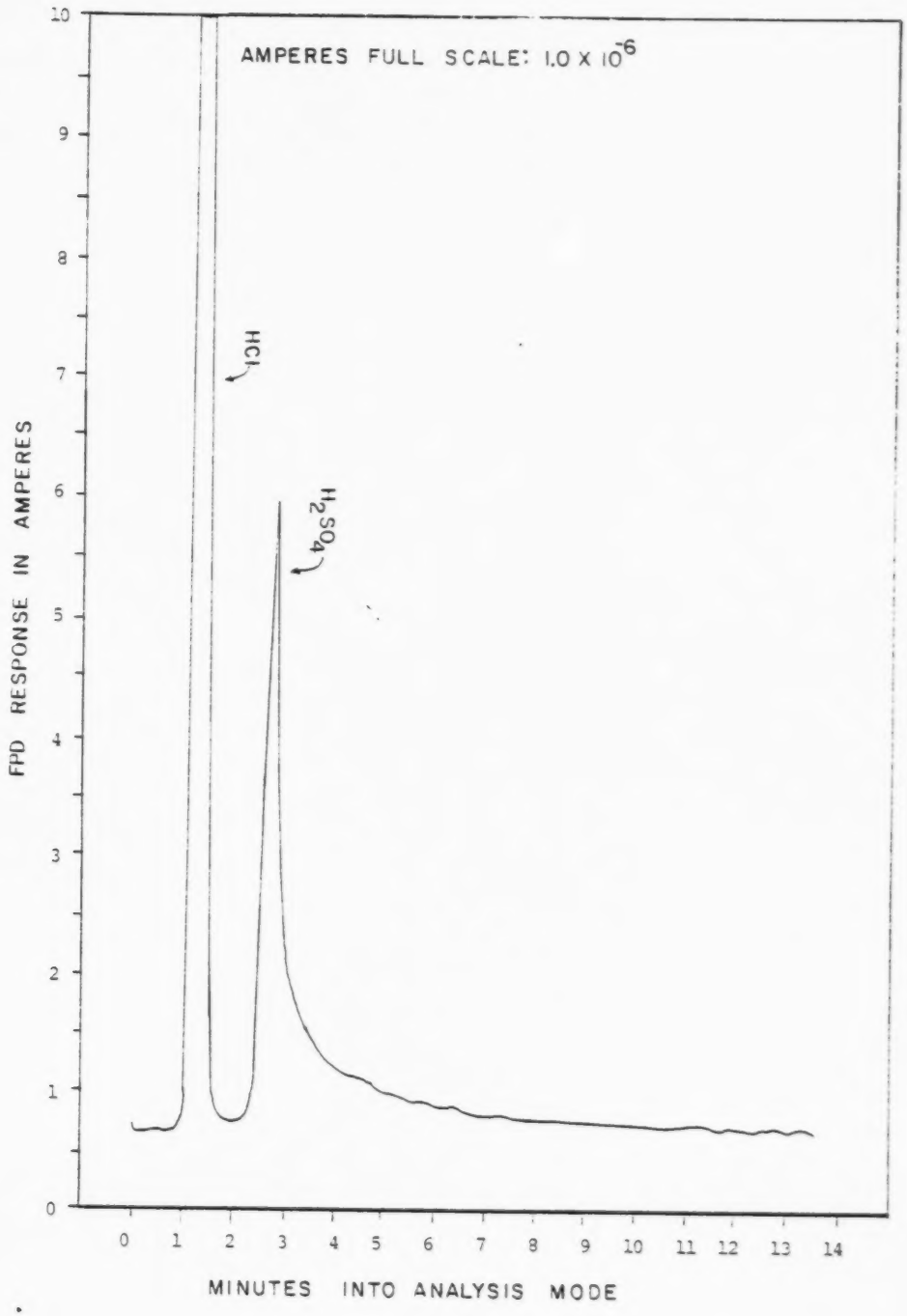

FIGURE A-6

COPY OF RAW DATA FOR SAMPLE NO. 31

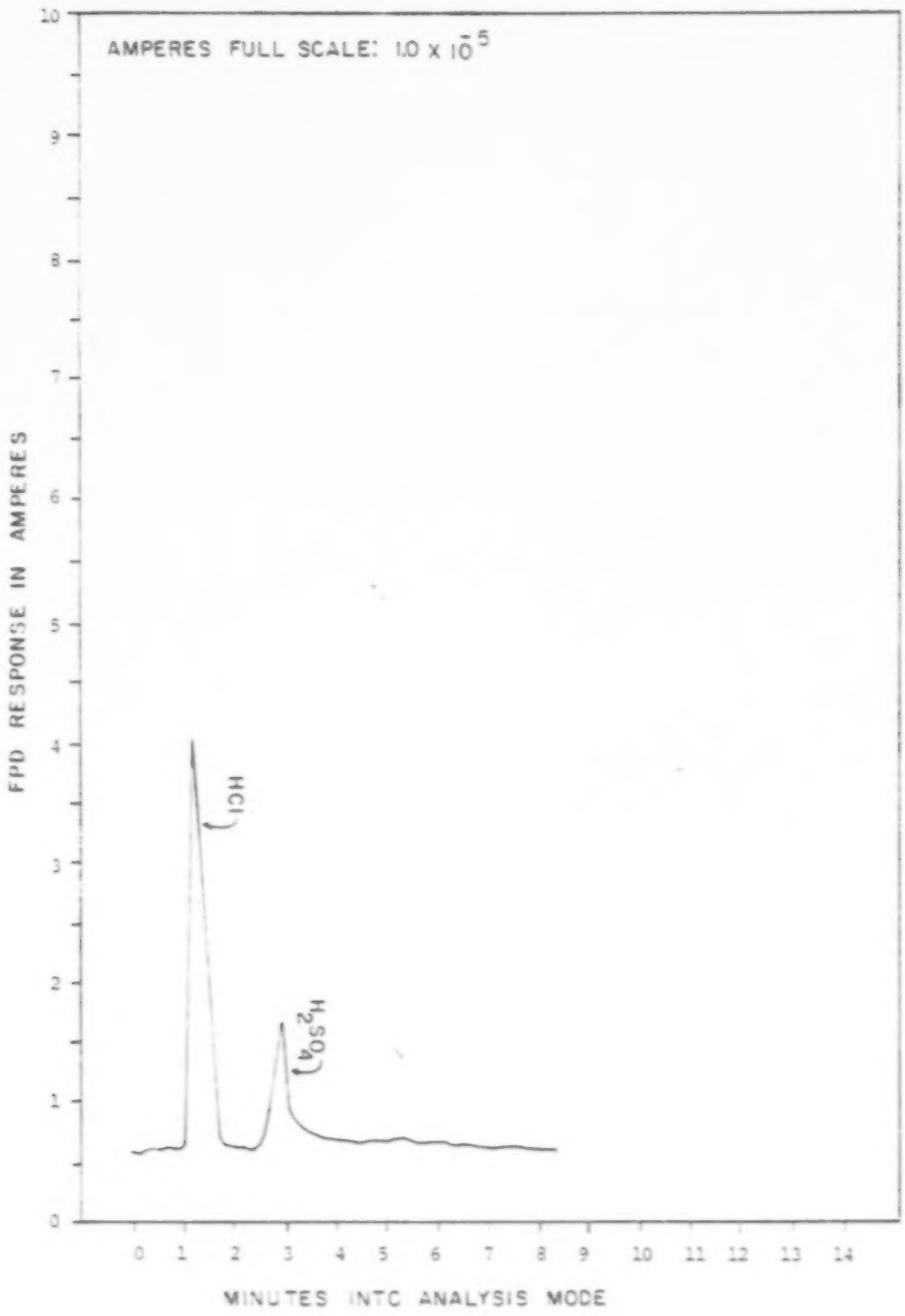

FIGURE A-7

COPY OF RAW DATA FOR SAMPLE NO. 35

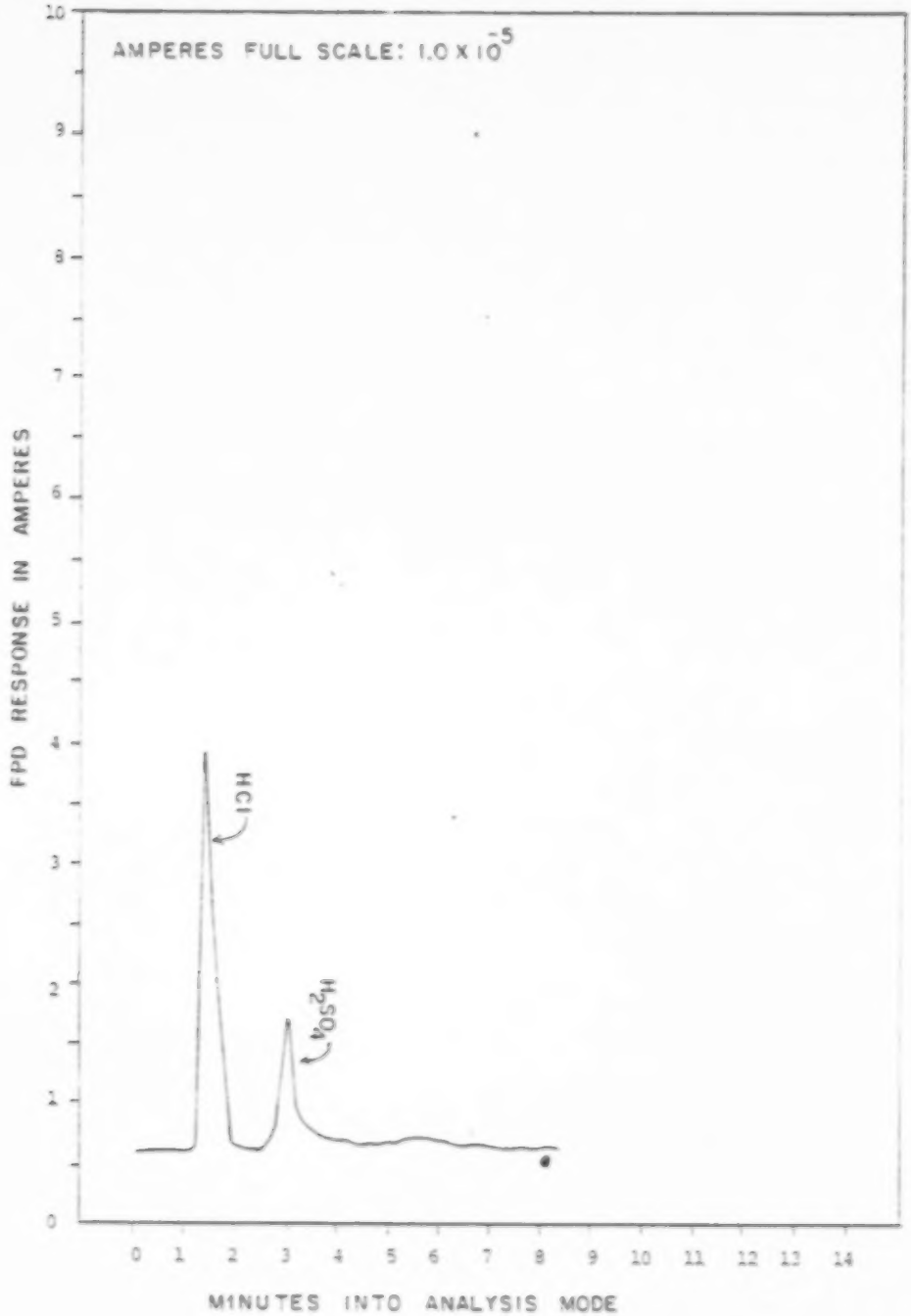

FIGURE A-8

COPY OF RAW DATA FOR SAMPLE NO. 36